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The late Dr. H. P. Talbot was Consulting Editor of the International Chemical Series from its inception in 1911 until his death in 1927.

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THE CHEMISTRY OF CELLULOSE AND WOOD

BY

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PREFACE

It is the aim of this book to cover completely the scientific and empirical data available on the chemistry of wood. This has necessitated the inclusion of cotton cellulose and its modified forms. Industrial processes are treated mainly from the side of the fundamental reactions involved. Perhaps owing to the insufficiency of our knowledge, these reactions receive but scant attention in most technical books. A thorough understanding of them, however, would remove pulping processes, *e.g.*, from the category of an art to that of a science. Many of the problems connected with the utilization of cellulose and wood cannot be solved by chemistry alone, so that there have been included certain chapters from the domain of biological chemistry and colloid science.

It is hoped that the usefulness of the book will be increased by the detailed statement of the conditions under which certain results were obtained. Mere statement of fact would, in the majority of cases, be meaningless. This policy has been pursued, also, for the reason that much of the original literature is difficult of access.

Cellulose, in its various forms, is the most abundant organic compound in the plant world and has been used by man since time immemorial. For a century or more, it has inspired cycles of chemical research, of varying intensity, the most pronounced being during the World War. At present, investigation is being pursued by so many workers, and from so many different angles, that it is to be hoped that interest will not flag until the important structural relationships are established. Lack of knowledge of the constitution of cellulose and lignin need occasion neither surprise nor impatience. The vast number of organic compounds has been largely produced from simple chemicals by synthesis. The research was prosecuted on the basis of chance and probability and was not hampered by knowledge of an existing sample which had to be duplicated or torn apart. Progress was from the simple to the complex, while with cellulose and lignin the reverse must be true.

The chemistry of cellulose and wood, of lignin particularly, is surrounded by a mass of data, largely speculative, which is much in need of weeding. But the information is so indefinite that he who performs the operation at this stage, may later awake to the embarassing fact that the grain rather than the tares have been uprooted. Categorical statements, however desirable, have accordingly been largely avoided. Réaumur could call a crocodile *un furieux insecte* to his own satisfaction, but not to that of the present generation.

A. W. SCHORGER

MADISON, WISCONSIN
June, 1926

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CHEMISTRY OF CELLULOSE AND WOOD

CHAPTER I

THE STRUCTURE, FORMATION, AND PHYSICAL PROPERTIES OF WOOD

In many trees the most prominent feature of the cross-section of the trunk is the separation into dark heartwood (duramen) and light sapwood (alburnum). In certain species, such as spruce, cottonwood, aspen, beech, and hackberry, there is little difference between the colors of heartwood and sapwood. Closer inspection shows that the wood, if grown in a temperate climate, consists of annual rings which are usually quite sharply defined. The inner portion of the ring, which is light in color, represents the growth produced in spring, and the dark outer portion that produced in summer. The dark summer wood is always more dense than the spring wood.

Wood is composed of hollow cells of various kinds, collectively known as wood elements. The cavity is known as the lumen. All cells, without doubt, perform a useful service, but in some cases their function is not clear. The minute structures of the two main classes of woods, gymnosperms (softwoods) and dicotyledons (hardwoods), differ greatly from each other.

Wood Elements.—Most of the cells in wood are long and narrow. Wood fibers (Fig. 1*e*), which are largely limited to hardwoods give strength and stiffness. Tracheids predominate in the conifers, where they perform the dual function of affording mechanical strength and conducting sap. Tracheids are polygonal in cross-section and arranged in radial rows. A characteristic feature of these elements is the presence of bordered pits. Holes or thin spots in the wall are known as pits; in shape these vary from slits to elliptical and round forms (Figs. 1*d* and 2*DE*). Elements have simple pits when their walls are parallel with the primary layer or middle lamella and bordered pits (Fig. 2*B*) when they diverge from it. The bordered pits are usually arranged in exactly similar position to pits in adjoining elements. The openings are closed by partitions which are extensions of the middle lamella. The partitions usually contain a thickened disk or torus. The portion of the membrane surrounding the torus is frequently perforated, as is proved by the fact that it is possible to force India ink through it.[1]

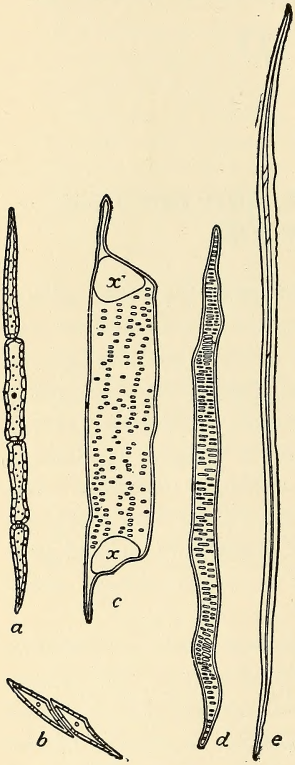


FIG. 1.—Isolated fibers and cells; *a*, four cells of wood parenchyma; *b*, two cells from a pith ray; *c*, a single joint of cell of a vessel, the openings *x* leading into its upper and lower neighbors; *d*, tracheid; *e*, wood fiber. (*After Roth.*)

The hardwoods contain cells of relatively large diameter superimposed to form a continuous tube, called a pore or vessel (Fig. 1*c*). These vessels serve to conduct sap from the roots to the leaves. The conifers do not have vessels, but the sap travels from one tracheid to another through the membrane of the pit. When the pores are of approximately the same size, as in maple and birch, the woods are known as *diffuse porous*, and when there are concentric rows of large and small pores, as in oak and elm, as *ring porous.*

The vessels of dicotyledons are frequently closed by tyloses. These are pith-like cells which are formed by intrusion into the lumen of the vessel of wood or ray parenchyma. Tyloses are rarely found in conifers except in the resin canals.

Medullary or pith ray cells (Fig. 1*a*) run in a procumbent position from the pith. They serve to conduct sap from the bark to the sapwood and *vice versa*, and to store starch.

---

[1] I. W. BAILEY, *Forestry Quart.*, **11** (1913), 12–20.

Parenchyma are short, thin-walled cells which occur in the xylem as scattered vertical rows, of which the upper and lower cells are tapered. These cells contain protoplasm and retain their power of subdivision after leaving the cambium. Their function is the same as that of the ray parenchyma cells.

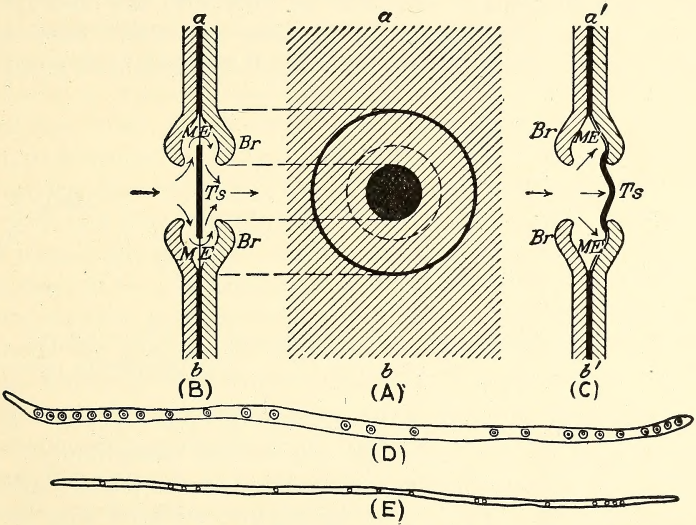


Fig. 2.—(*A*) Piece of radial wall of a tracheid showing a bordered pit in surface view. Part of the dark-colored torus or thickened portion of the pit membrane may be seen through the opening in the wall. This pit orifice is surrounded or bordered by the embossed portion of the secondary wall. (*B*) Section cut through (*A*) at *a–b*, showing embossed wall seen in (*A*) and that of cell directly under it. The membrane and torus occupy a median position. (*C*) Section showing the valve-like action of the torus. (*Br*) Bordered area, (*ME*) membrane, (*Ts*) torus. (*D*) Tracheid from spring-wood. (*E*) Tracheid from summer wood. The tracheids have their pitted radial walls uppermost. (*After Bailey.*)

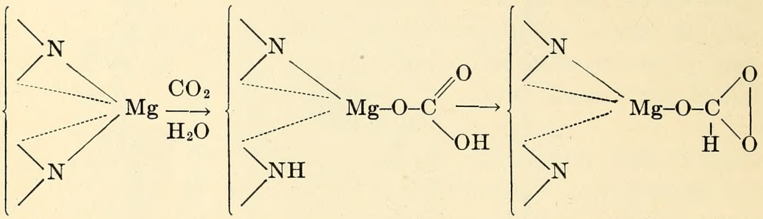
Formation of Wood.—The structural membranes of the higher plants are formed from the carbon dioxide of the air by the aid of light. The first acceptable working hypothesis of photosynthesis was that of Baeyer.[1] He assumed that when sunlight strikes chlorophyll which is surrounded by carbon dioxide the latter is decomposed into oxygen, which is liberated, and carbon monoxide, which remains combined with the chlorophyll. The carbon monoxide was reduced to formaldehyde, which polymerized to sugar.

---

[1] A. Baeyer, *Ber.*, **3** (1870), 68.

$$CO + H_2 = H.CHO.$$
$$6H.CHO = C_6H_{12}O_6.$$

A step in advance was the opinion of Hoppe-Seyler[1] that the carbon dioxide actually combined as such with the chlorophyll to form a loose compound. Willstätter and Stoll[2] have confirmed this view. The chlorophyll-formaldehyde-peroxide breaks up into chlorophyll, formaldehyde, and oxygen. It is probable that the formaldehyde polymerizes immediately.



Chlorophyll   Carbon dioxide compound of chlorophyll   Chlorophyll-formaldehyde-peroxide

A very large literature has accumulated on the photosynthesis of carbohydrates. There is no satisfactory evidence that in the living plant the process passes through the formaldehyde stage, though the detection of formaldehyde has been reported. Baly[3] and his associates found that when an aqueous solution of carbon dioxide was exposed to ultra-violet light of wave length $200\mu\mu$ formaldehyde was produced; this, in turn, was polymerized to reducing sugars at wave length $290\mu\mu$. Both processes occur simultaneously in the light of a quartz mercury lamp, so that formaldehyde cannot be detected except by removing it with a stream of carbon dioxide or preferably by the addition of substances which absorb the polymerizing light of wave length $290\mu\mu$. The reaction is reversible in the unscreened light of a quartz mercury lamp and the equilibrium lies far towards the side of carbon dioxide. In the presence of a photocatalyst such as chlorophyll the equilibrium is reversed and thrown to the side of the reducing sugar. This explains the difficulty encountered in detecting formaldehyde as an intermediate product.

---

[1] F. Hoppe-Seyler, "Physiologische Chemie," Berlin (1881), p. 139.

[2] R. Willstätter and A. Stoll, "Untersuchungen über die Assimilation der Kohlensaure," Berlin (1918), p. 244.

[3] E. C. C. Baly, I. M. Heilbron, and W. F. Barker, *J. Chem. Soc.*, **119** (1921), 1025–1035; *J. Soc. Chem. Ind.*, **40** (1921), 377–379R.

The syrup obtained by the polymerization of formaldehyde by ultra-violet light[1] contained about 10 per cent of a hexose sugar.[2] Polysaccharides and anhydro-sugars were absent.

The method whereby the cell walls are built up from the simple products of photosynthesis in the leaf is far from clear. The secondary wood, which constitutes almost all of the wood of the stem, is produced in the cambium layer, which is situated between the cortex and the last layer of sapwood. The cambium cells are soft and thin walled; each contains protoplasm, a nucleus, and organic and inorganic constitutents essential to growth. The first stage in the multiplication of the cell consists in the splitting of the nucleus and the formation of protoplasmic spindle fibers between the nuclei. These enlarge at the middle to form a cell plate, which splits to produce the plasma membrane of the two daughter cells. Between these membranes is secreted a substance indistinguishable from lignin in the mature cell, which forms the primary layer or middle lamella. Upon the middle lamella are deposited layers of cellulose intermingled with lignin.

One of the cells forms bark or wood, while the other is left to undergo further subdvision. An annual ring in the radial direction may represent as many as 100 wood elements. The cells reach full development rapidly and then die.

Wislicenus[3] has advanced the theory that growth of the cell wall takes place by adsorption of colloids from the sap of the cambium. Cellulose is first formed as a chemically indifferent framework possessing a large surface, which is thickened by adsorption of a mixture of colloids to produce lignin. Experimental work was performed with sap obtained by tapping. Before the period of foilage development the amount of colloids in the sap is small and increases slightly during the period of wood formation. Only 3.5 to 8.4 per cent of the weight of the total solids in the spring sap of birch consisted of colloids. This was determined by adsorbing the colloids by shaking with alumina, filtering, and determining the solids in the filtrate. Of the total solids in the sap of sugar maple only 4.4 per cent were colloids, while that of hornbeam contained 21.08 per cent before the period of leaf formation. The fresh sap gave no reaction for starch with iodine solution and no reaction for lignin.

---

[1] E. C. C. Baly, *J. Ind. Eng. Chem.*, **16** (1924), 1016–1018.

[2] J. C. Irvine and G. V. Francis, *J. Ind. Eng. Chem.*, **16** (1924), 1019–1020.

[3] H. Wislicenus and M. Kleinstück, *Kolloid-Z.*, **6** (1910), 17–23, 87–94; H. Wislicenus, *Ibid.*, **27** (1920), 209–223; *Cellulosechemie*, **6** (1925), 45–58.

The sap of the birch contained the following total solids and colloids:

Date	Solids per 100 cubic centimeters, grams	Amount adsorbed, per cent
March 12	0.6070	4.45
April 15	0.6964	6.70
April 23	1.2238	8.30
May 26	0.4154	37.07
July 27	0.2292	19.55

It is not at all apparent how the theory of Wislicenus can be applied to the growth of the cell wall. The amount of colloids in the sap is low and it is unlikely that they can penetrate, in quantity, either the middle lamella or the plasma membrane in which the vital syntheses take place. All the evidence points to the presence of protoplasm at every point where growth takes place; hence it is most probable that transformation of sugars into colloids and formation of the cell wall take place simultaneously at the middle lamella-plasma membrane interface. Casparis[1] considers it improbable that incrustation with lignin takes place through adsorption of external material by the cell membrane. It is more likely that lignin is formed *in situ* from carbohydrates.

It is desirable to follow the migration of the carbohydrates from the leaf. The starch formed in the leaf by photosynthesis is converted into sucrose, ostensibly by enzymes, and transported downward to the growing cells through the sieve tubes of the cortex. Neither the flow of water upward in the sapwood or of sap downward in the cortex has been satisfactorily explained. Diffusion can play but a minor part in the transportation of foodstuffs. It would require 2 years and 7 months for 1 milligram of sucrose to travel from a 10 per cent solution a distance of 1 meter.[1] Starch as such is not transportable. The sugar, after reaching the ray cells and wood parenchyma, may be reconverted into starch and held in reserve.

---

[1] P. Casparis, *C. A.*, **15** (1921), 1333.

An investigation by Jones[2] on the storage of sugar in the maple is particularly illuminating as to the probable method of growth of the cell wall. Maple sap, as it flows from the tree, is rich in sucrose but practically free from reducing sugars; if the wood is ground and extracted with water, approximately one-half of the sugar obtained consists of reducing sugars. When water is forced through a section of wood, sucrose can be washed out, but not reducing sugars. This shows conclusively that sucrose is stored in the pores and reducing sugars in the cell sap of the living cells. It would, accordingly, appear that the synthesis of constituents of the cell wall begins with carbohydrates no higher than *monoses*.

Lignification.—A study of the lignin content of rye straw shows that a large amount of lignin is present in the early stages of growth.[3] Rye stalks 10 days after planting in summer contained 11.6 per cent of lignin and this value increased to 14.5 per cent in 8 weeks. The change in lignin and methoxyl in the stem of rye sown in October is shown below. It would appear that cellulose and lignin are formed simultaneously; furthermore, since lignification increases with age it is probably not due to adsorption of colloids from without, as the cell wall would be expected to decrease in permeability as it approached maturity.

	Age, in days					
	192	223	231	239	253	274
Lignin (Willstätter), per cent	13.03	17.24	18.57	18.86	19.07	20.49
CH_3O in lignin, per cent	3.03	11.46	13.41	12.84	13.38	13.42

---

[1] H. de Vries, *Botan. Z.*, **43** (1885), 1.

[2] C. H. Jones, *J. Assoc. Official Agr. Chem.*, **2** (1916), 103–111.

[3] E. Beckmann, O. Liesche, and F. Lehmann, *Biochem. Z.*, **139** (1923), 502.

Little reliance can be placed on staining with zinc chloriodine as a measure of lignification. Potter[1] found that in numerous woods, sections of the cell wall gave the blue color of cellulose. This was particularly true after boiling the sections in water; the wood of *Æsculus* after boiling in water showed bluish-violet layers in nearly all the fibers and cells. Spaulding[2] found that when the wood of *Populus* was stained immediately after felling the thick inner layer of the cell was invariably stained blue.

The function of lignin is generally assumed to be physical. According to Sachs,[3] lignification produces an increase in the hardness of the cell membrane and a decrease in extensibility; it permits the membrane to be easily penetrated by water without swelling appreciably. Sonntag[4] found that the ability of fibers to swell in water, particularly in cross-section, decreased with the degree of lignification. Tracheids of *Abies pectinata* increased 14.8 per cent in cross-section from the air-dry condition, while fibers of pure linen increased 55.5 per cent. Lignification produces decrease in ductility and tensile strength.

Lignification, aside from increasing the hardness of the cells, renders them more resistant to crushing and bending.[5]

Schellenberg,[6] on the other hand, has held that a membrane is not changed in its mechanical properties by lignification, but shows the same gradations in the magnitude of its strength, extensibility, and ability to swell as unlignified fibers. The physical significance of lignification lies in the fact that a lignified membrane is no longer capable of growth. Lignification always takes place at a time when the cell contains a living plasma. The cell wall having become lignified, it no longer shows surface growth and apparently no increase in thickness; the cell is no longer capable of division.

It is now known that the amount of lignin present in a wood has no direct relation to its mechanical properties. In general, the best single criterion for strength is specific gravity. That a wood, such as bald cypress, having a high lignin content, need not necessarily have high mechanical properties is shown in the following table:

---

[1] M. C. Potter, *Ann. Botany,* **18** (1904), 121–140.

[2] P. Spaulding, *Rept. Missouri Botan. Gardens,* **17** (1906), 58.

[3] J. Sachs, "Lehrbuch der Botanik," 4 Aufl., Leipzig (1874), p. 21.

[4] P. Sonntag, *Landw. Jahrb.,* **21** (1892), 839–869.

[5] F. Lukas, *Akad. Wiss. Wien,* **85,** I (1882), 292–327; **87,** I (1883), 303–327; *cf.* T. von Weinzierl, *Ibid.,* **76,** I (1877), 385–461.

[6] H. Schellenberg, *Jahrb. wiss. Botanik,* **29** (1896), 237–266.

	Lignin,[1] per cent	Specific gravity	Modulus of rupture,[2] pounds per square inch	Modulus of elasticity, pounds per square inch	Hardness, oak = 100
Bald cypress	33.9	0.45	7,110	1,378	34
Yellow poplar	23.2	0.37	5,570	1,207	32
Yellow birch	26.3	0.55	8,810	1,490	70

[1] G. J. Ritter and L. C. Fleck, J. *Ind. Eng. Chem.*, **15** (1923), 1055.
[2] H. S. Betts, "Timber," N. Y. (1919).

Growth and Structure of Cell Wall.—In 1853, von Mohl[1] expressed the opinion that the wall grows by apposition, *i.e.*, the deposition of substances in successive layers. Nägeli, as a result of his study of the growth of starch grains[2] and the cell wall,[3] concluded that the cell wall consists of ultramicroscopic, crystalline, molecular complexes which he called micellæ. By this assumption he was able to explain striation, stratification, swelling, double refraction, and other properties of the cell wall.

Each micella is normally surrounded by a film of water, but in the dry condition the micellæ form a continuous membrane. Swelling takes place up to the point where the pressure of the aqueous layers equals the cohesion between the micellæ. The smaller the micellæ the greater is their attraction for water. The attraction of the micellæ for water decreases relatively more rapidly than that between micellæ. The water closest to the micellæ is most firmly held, while this attraction decreases at a distance to such an extent that some of the water is merely held by capillarity in the spaces created by swelling. The spiral arrangement of the micellæ explains why shrinking and swelling occur laterally and not longitudinally.

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[1] H. von Mohl, *Botan. Z.*, **11** (1853), 753, 769; **16** (1858), 373.

[2] C. W. Nägeli, "Die Stärkekorner," Zurich (1858), 623 pp.

[3] C. W. Nägeli, *Beitr. Wiss. Botan.*, **3** (1863), 1–126; C. W. Nägeli and S. Schwendener, "Das Mikroskop," 2 Aufl., Leipzig (1877), 679 pp.

Nägeli[1] assumed that the cell wall grew by intussusception, that is, the new micellæ were formed between the old. The old micellæ gradually increased in size, whereby their ability to hold water gradually decreased. Growth by intussusception has been disputed in numerous papers, but there is now general agreement that it usually takes place in this way, though occasionally by apposition, or both. Nägeli's general conception of the structure of the cell wall must be viewed as a great intellectual achievement and as the most satisfactory yet proposed.

The micellar theory has been applied to dyeing.[2] The penetration of dyes and mordants into the interstices between the micellæ is limited to particles of a diameter less than $1\mu\mu$. When the fibers have been mercerized larger particles can be absorbed, since the size of the interstices is increased. Röntgen-ray examination in the wet and dry state of normal cellulose, mercerized fibers, and threads produced from viscose and a cuprammonium solution of cellulose shows no definite change in the lattice of the crystals as a result of swelling.[3] The change produced is accordingly intermicellar.

Another theory of the structure of the cell wall is of passing interest. Wiesner[4] thought that the cell wall was formed of round microscopic bodies which he called dermatosomes. These were obtained under oxidizing and hydrolytic conditions, whereby the fibers were converted into brittle oxycellulose or hydrocellulose. So far as known, these fragments have no bearing on the structure of the wall.

In recent years there has been much ingenious though fanciful speculation on rhythmic growth. Liesegang[5] found that, when a drop of concentrated silver nitrate solution was placed on a gelatin plate containing potassium bichromate, formation of silver chromate did not take place uniformly, but in the shape of concentric rings. No adequate explanation has so far been offered for the phenomenon. Kuster[6] has attempted to explain the growth of wood as due to banding in a colloidal medium. When the end of a cylinder of gelatin was immersed in silver nitrate he obtained not only rings but ascending spiral bands of silver chromate. In this connection Balls[1] has noted that when a cotton hair is swelled to five to ten times its normal thickness with sodium hydroxide and carbon bisulphide, as many as 25 daily growth rings become visible under the microscope. The thickness of each ring is about 0.4μ.

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[1] C. W. Nägeli, *l.c.*; "Ueber das Wachsthum der Stärkekorner durch Intussusception," *Botan. Mitt.*, **3** (1881), 487–534.

[2] R. Haller, *Kolloid-Z.*, **20** (1917), 127–145.

[3] J. R. Katz, *Z. Physik*, **25** (1924), 321–326.

[4] J. Wiesner, *Akad. Wiss. Wien*, **93**, I (1886), 17–80.

[5] R. Liesegang, "Chemische Reaktionen in Gallerten," Leipzig (1898).

[6] E. Kuster, "Ueber Zonenbildung in kolloidalen Medien," Jena (1913).

Physical Effects of Water.—Water occurs in wood as "free" water in the cell cavities and as "imbibed" water in the cell walls. Some of the water must be colloidally bound with the fibers. The natural state is a condition wherein the cell walls

FIBER SATURATION POINTS DETERMINED BY COMPRESSION TESTS[1]
(Results based on the dry weight of the wood)

SPECIES	MOISTURE (AVERAGE), PER CENT
Longleaf pine, green	25
Red spruce, green	31
Chestnut, green	25
Loblolly pine:	
Heartwood, green	23
Heartwood, air dry	24
Sapwood, green	24
Sapwood, air dry	26
Norway pine:	
Heartwood, green	30
Sapwood, green	28
Tamarack, green	30
Western hemlock, green	29
Red fir, green	23
White ash, green	20
Red gum, air dry	25
Red spruce:	
Air dry	30–32
Superheated	24–25
Tamarack:	
Air dry	30–32
Superheated	24–25
Chestnut:	
Air dry	26–27
Superheated	22–24

[1] H. D. TIEMANN, *Forest Service Circular*, 108 (1907); "The Kiln Drying of Lumber," N. Y. (1917), p. 104.

[1] W. L. BALLS, *Proc. Roy. Soc.*, **90B** (1919), 542–555.

are saturated with water; this is known as the *fiber saturation point.* There is no sharply defined method for determining this point. The methods usually employed are based on the observation that as soon as the water falls below the fiber saturation point the wood begins to shrink and increase in strength. The logical procedure would be to expose the wood to an atmosphere of 100 per cent humidity until the cell walls are saturated; however, the method is complicated by the condensation of water on the surface of the wood, so that free water is present. The fiber saturation point varies from 20 to 30 per cent of the dry weight of the wood. The results obtained by compression tests are shown in the accompanying table.

The influence of the density of wood and its resin content on hygroscopicity has been investigated by Zeller.[1] In all cases where the specific gravities lay between 0.41 and 0.80, and the resin contents were small, the curves for hygroscopic moisture were the same up to a certain point from which they diverged according to the density of the wood. At a relative humdity of 94.75 to 96 per cent, the less dense woods took up the greatest amount of moisture. This is explained on the assumption that

Moisture in Shortleaf Pine Sapwood Shavings at Various Humidities and at 25°C.

Sp. gr. 0.41		Sp. gr. 0.61		Sp. gr. 0.69	
Moisture in shavings, per cent	Relative humidity, per cent	Moisture in shavings, per cent	Relative humidity, per cent	Moisture in shavings, per cent	Relative humidity, per cent
4.12	11.0	2.5	6.6	3.0	7.5
7.80	33.2	7.9	35.8	7.88	34.6
9.00	49.5	9.2	47.5	9.7	53.0
10.80	60.4	10.4	61.3	10.75	62.5
15.50	81.0	16.2	82.2	15.3	79.3
18.75	90.0	20.0	90.0	19.3	91.0
23.80	95.5	24.25	96.0	23.4	95.3
27.60	97.5	26.00	97.4	25.0	97.5
30.25	98.7	27.60	98.7	26.25	98.8
34.00	100.0	29.88	100.0	28.00	100.0

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[1] S. M. Zeller, *Ann. Missouri Botan. Gardens,* **7** (1920), 51–74.

at and above this point moisture is condensed and absorbed on the surface of the fibers. The point of divergence of the curves accordingly represents the fiber saturation point. The fiber saturation points for longleaf and shortleaf pine determined in this way were:

	Heartwood moisture, per cent	Sapwood moisture, per cent
Longleaf pine	23.25	23.75
Shortleaf pine	24.5	24.25

Resin has little influence on hygroscopic moisture until the humidity approaches 100 per cent. At 100 per cent humidity, heartwood of longleaf pine of sp. gr. 0.51 showed a hygroscopicity of 33.2 per cent, while wood of sp. gr. 0.86 to 0.94 with 18.4 per cent resin showed a hygroscopicity of 21.12 per cent.

Beadle[1] appears to have first observed that the exposure of dry cellulose to water or its vapor produced a pronounced rise in temperature. The more finely divided the cellulose the more rapidly it took up moisture, but the coarse cellulose eventually took up more moisture than the fine. Two grams of cotton wool dried at 220°F. showed a rise of 4.8°F. after an exposure of 15 minutes to moist air. The temperature rose more rapidly when air was blown against the cotton. He attributed the phenomenon to "hydration," since the cotton remained at a temperature greater than its surroundings as long as it was taking up moisture.

EVOLUTION OF HEAT WITH STARCH AND WATER

WATER TO 100 GRAMS OF DRY STARCH, GRAMS	HEAT PER GRAM OF DRY STARCH, CALORIES
0.23	28.11
2.39	22.60
3.23	20.97
8.16	12.43
12.97	7.37
15.68	5.21
19.52	2.91

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[1] C. BEADLE, *Nature*, **49** (1894), 457; *Chem. News*, **71** (1895), 1–2; C. BEADLE and O. W. DAHL, *Ibid.*, **73** (1896), 180–183.

Rodewald[1] has determined the heat evolved when starch containing various amounts of water swells in water.

Masson[2] explained the rise in temperature as due to the formation of a solid solution, or what Travers[3] prefers to call a "rigid" solution. Chemical combination and condensation on the surface of the fiber are not directly involved. The rise and fall of the temperature curves are similar in water vapor and water; in both cases the rise in temperature is due to condensation on the cotton of water vapor which is absorbed. The water probably undergoes osmotic diffusion into the fiber to form a solid solution whose vapor pressure is always lower than that of water. This is in accordance with Trouton's[4] observation that cotton containing a definite proportion of water behaves like an aqueous solution in that at different temperatures it shows a vapor tension which is a constant fraction of that of pure water. When cotton is plunged into water the air adhering to the fibers maintains the space necessary for the occurrence of *distillation* of the water, the vapors then condensing on the cotton.

A rise in temperature is not peculiar to cellulose. In 1822, Pouillet[5] observed that when a powder was moistened with a liquid in which it did not dissolve there was a rise in temperature. Dry charcoal and silica will develop about 18 calories per gram when treated with water.[6] Parks[7] states that the heat evolved is proportional to the area of the surface exposed by the solid, and that the amount of heat developed per square centimeter is approximately 0.00105 calorie when the temperature is near 7°. According to Martini,[8] the surface exposure does not always explain the marked rise in temperature. He compares the Pouillet effect to a kind of "inverted solution."

Dunlap[9] found that dry sugar maple, beech, and longleaf pine liberated 16.6 to 19.6 calories per gram when in contact with water. In drying wood it is, accordingly, necessary to furnish this amount of heat to overcome the attraction of the wood for moisture.

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[1] H. Rodewald, *Z. physik. Chem.*, **24** (1897), 206.

[2] O. Masson, *Proc. Roy. Soc.*, **74** (1905), 230–255.

[3] M. W. Travers, *Proc. Roy. Soc.*, **79A** (1907), 204–205.

[4] F. T. Trouton, *Proc. Roy. Soc.* **77A** (1906), 292.

[5] Pouillet, *Ann. chim. phys.*, [2] **20** (1822), 141–162.

[6] T. Martini, *Phil. Mag.*, [5] **50** (1900), 618–619.

[7] G. J. Parks, *Phil. Mag.*, [6] **4** (1902), 247.

[8] T. Martini, *Phil. Mag.*, [6] **5** (1903), 595–596.

[9] F. Dunlap, Unpublished Report, Forest Products Laboratory.

The hygroscopicity of absorbent cotton has been determined by Masson and Richards[1] by exposing it over sulphuric acid of constant vapor pressure. The cotton was brought to constant weight by exposure to phosphorus pentoxide for 24 hours. The results are given in the table below. The hygroscopic moisture present in cotton at a humidity of 97.2 per cent was 17.70

HYGROSCOPICITY OF COTTON OVER SULPHURIC ACID SOLUTIONS

H_2SO_4 Per cent	$\frac{p}{P}$	M_A	M_E	M	$\frac{M}{W}$
73.8	0.050	0.0120	0.0145	0.0132	0.0139
67.0	0.100	0.0175	0.0198	0.0186	0.0196
59.0	0.198	0.0264	0.0311	0.0288	0.0304
52.6	0.294	0.0356	0.0406	0.0381	0.0402
47.2	0.408	0.0441	0.0497	0.0469	0.0495
43.1	0.500	0.0509	0.0593	0.0551	0.0581
40.5	0.556	0.0530	0.0655	0.0592	0.0624
38.8	0.598	0.0599	0.0690	0.0644	0.0679
32.3	0.710	0.0716	0.0840	0.0778	0.0821
26.8	0.794	0.0860	0.1002	0.0931	0.0982
23.2	0.844	0.0989	0.1107	0.1048	0.1106
20.3	0.874	0.1045	0.1250	0.1148	0.1210
18.1	0.894	0.1114	0.1300	0.1207	0.1274
10.3	0.952	0.1378	0.1606	0.1492	0.1574
6.2	0.972	0.1563	0.1792	0.1678	0.1770

W = weight (0.948 gram) of dry cotton.
T = temperature (20°) of the apparatus.
p = actual pressure of water vapor in the atmosphere employed.
P = saturation pressure of water vapor at the same temperature.
M_A = weight of moisture absorbed by the cotton after exposure in the apparatus till further absorption appears negligible.
M_E = weight of moisture retained by the sample after it has been supersaturated by exposure over water and then allowed to evaporate in the apparatus till further loss appears negligible.
M = arithmetic mean of M_A and M_E; taken as indicating the amount of absorbed moisture which is required to establish true equilibrium.

The per cent of absorbed water is obtained by multiplying the last column by 100.

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[1] O. MASSON and E. S. RICHARDS, *Proc. Roy. Soc.*, **78A** (1906), 412–429.

per cent. According to the authors, the true absorption value can be obtained only by taking the mean of the apparent equilibrium values reached by absorption and evaporation. Either change can be followed by observing the characteristic temperature as given by a thermometer. According to Rakovski,[1] cellulose loses water more slowly than it absorbs it. The maximum hysteresis is 1.8 per cent of water.

Fenchel and Cornely[2] working with paper and paper pulps found that moisture was absorbed more rapidly than it was lost. The initially rapid absorption of moisture in a saturated atmosphere decreased greatly in rate and was not complete in 14 days; after 17 days at a temperature of 18° (± 0.5°), cotton absorbed 16.5 per cent of water and spruce mechanical pulp, 22.35 per cent. According to Scheurer,[3] dry, bleached cotton will take up 19.0 to 20.2 per cent of water from an atmosphere saturated with water vapor.

Wood shows considerable variation in hygroscopicity between species, cotton having an intermediate value.[4]

Browne[5] found that cellulose absorbed only 12.57 per cent of water after exposure at 20° for 25 days in an atmosphere of 100 per cent humidity. This datum is abnormal.

Absolutely dry cellulose is stated to be the most hygroscopic substance known. It will take up 3 per cent of moisture from all known drying agents.[6]

The amount of water absorbed is influenced by the temperature and humidity of the surrounding atmosphere, and various other factors. The water-soluble constituents of cotton took up 28.71 per cent of moisture in comparison with 8 per cent for cotton under the same conditions. Heating[7] cellulose above 100°

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[1] A. V. Rakovski, *J. Russ. Phys.-Chem. Soc.*, **47** (1915), 18–21; *cf.* A. R. Urquhart and A. M. Williams, *J. Textile Inst.*, **15** (1924), 138; T. Kujira *et al.*, *J. Soc. Chem. Ind.*, **43** (1923), 894A.

[2] K. Fenchel and R. Cornely, *Wochbl. Papierfabr.*, **44** (1913), 4323–4327.

[3] A. Scheurer, *Bull. Mulhouse*, **87** (1921), 129–135.

[4] H. D. Tiemann, "The Kiln Drying of Lumber," 3rd ed. (1920), p. 105.

[5] C. A. Browne, *J. Ind. Eng. Chem.*, **14** (1922), 712; *cf.* R. E. Wilson and T. Fuwa, *Ibid.*, p. 913.

[6] H. Jentgen, *Z. angew. Chem.*, **23** (1910), 1544.

[7] J. H. Lester, *J. Soc. Chem. Ind.*, **21** (1902), 388–389.

reduces the hygroscopicity.[1] Cotton cloth which has been thoroughly dried will not regain the amount of moisture held in the air-dry state even after long exposure to the atmosphere.[2] Complete drying by the aid of heat appears to produce a state of partial irreversibility, so that hygroscopicity should always be determined with material dried at low temperatures. The hygroscopicity of wood is reduced by heating in air or steam at temperatures above 100°.[3]

The absorption of moisture has been explained as a case of solid solution. It is a general law in chemistry that like dissolves like. Cellulose with its hydroxyl groups shows a pronounced affinity for substances, such as water and alcohol, which contain a hydroxyl group. Stradnikov[4] has shown that water requires several months to displace alcohol from cellulose at the ordinary temperature. Shrinkage of wood may be considerably reduced by the Powell process, wherein the wood is impregnated with a solution of molasses or sucrose, dried, and heated at 120° to produce caramelization. Concentrated solutions of sucrose contain large colloidal aggregates and are adhesive until crystallization sets in.[5] Crystalline sugar can penetrate the cell wall and subsequent caramelization would change it to a state of rigid, colloidal dispersion. Reduction in shrinkage may be due to mechanical resistance offered by colloidal sugar, but it is more probable that there is formation of a solid solution whereby the sugar partially satisfies the attraction of the cellulose for water.

Wood in swelling exerts a pressure sufficient to crush the fibers transversely. This pressure in even the weakest wood is over 200 pounds per square inch. The Egyptians are stated to have split stone by drilling holes and inserting dry wooden wedges which were then moistened with water.[6] The pressures exerted by some colloids is enormous. According to Rodewald,[7] 1 gram of starch can develop a pressure of 2523 atmospheres on swelling in water.

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[1] W. Will, *J. Soc. Chem. Ind.*, **34** (1905), 148.

[2] S. H. Higgins, *J. Soc. Chem. Ind.*, **28** (1909), 188; J. Hübner and F. Teltscher, *Ibid.*, **28** (1909), 644.

[3] H. D. Tiemann, "The Kiln Drying of Lumber," (1917), p. 260.

[4] G. L. Stradnikov, *J. Russ. Phys.-Chem. Soc.*, **48** (1916), 301.

[5] H. Wislicenus, *Cellulosechemie*, **6** (1925), 57.

[6] G. Rawlinson, "History of Ancient Egypt."

[7] H. Rodewald, *Landw. Vers.-Sta.*, **45** (1895), 227.

The radial shrinkage of most woods varies from 2 to 8.5 per cent, and the tangential from 4.2 to 14 per cent. The lower shrinkage radially is due to the arrangement of the medullary ray cells at right angles to the axis of the tree. The longitudinal shrinkage is very slight; this holds for masses as well as for individual fibers. Koehler[1] states that theoretically the cell walls are made of fibrils which run spirally in the cell walls. The water is held almost entirely between these fibrils. The fibrils are ultramicroscopic, but their probable orientation can be determined by the direction of checks and other markings in the cell wall. These spirals usually run nearly parallel to the axis of the cell; as the water leaves the spaces between the fibrils they draw together in a direction almost at right angle to the axis. This action results in a considerable transverse shrinkage, but in slight longitudinal shrinkage. His theory of the structure of the cell wall and its behavior with water closely resembles the micellar theory of Nägeli; the latter was able to render visible the spiral striations in cells of *Abies excelsa* by swelling them in concentrated sulphuric acid.[2]

The manner in which moisture travels through wood is unknown. It appears to pass in the form of a vapor from one cell wall to the other, where it condenses and the process is repeated. Beams 12 inches square and 16 feet long require about 2 years of air drying before the moisture in the interior falls to the fiber saturation point.[3]

Density.—Dunlap[4] has found the average density of wood substance to be 1.54. There are appreciable differences between species as shown in the following table:

Longleaf pine	1.5060	Beech	1.4990
Douglas fir	1.5639	Red oak	1.5395
Pacific yew	1.5534	Sugar maple	1.5506

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[1] A. Koehler, "The Properties and Uses of Wood," N. Y. (1924), p. 50.

[2] C. W. Nägeli and S. Schwendener, "Das Mikroskop" 2 Aufl., Leipzig (1877), p. 536.

[3] H. D. Tiemann, *Forest Service Bull.*, **70** (1906), 123.

[4] F. Dunlap, *J. Agr. Research*, **3** (1914), 423–428.

The results were obtained by determining the density of the solution of calcium nitrate in which the wood would remain in suspension. The method is obviously inaccurate, since the fibers would not absorb the calcium nitrate solution as such but water preferentially.

Richter[1] determined the density of wood and wood pulps in alcohol in a pycnometer. The density of the pulps varied from 1.408 to 1.634. Pure cellulose had a density of 1.583. The values for three species of American woods were:

Black spruce (*Picea americana*)	1.512
White spruce (*Picea canadensis*)	1.517
Balsam, heartwood (*Abies fraseri*)	1.402

De Mosenthal[2] gives the density of wood cellulose as 1.575 and of cotton as 1.61. Apparently, the density of the encrusting substances is less than that of cellulose. The great variations in densities reported for both wood and cellulose indicate the necessity for further investigation.

The specific gravity of some common American woods in the oven-dry state are given below:

APPARENT SPECIFIC GRAVITIES OF SOME AMERICAN WOODS

	Specific gravity		Specific gravity
Ash, white	0.60	Cedar, white	0.32
Aspen	0.42	Cypress, bald	0.47
Basswood	0.40	Fir, Douglas	0.52
Beech	0.66	Hemlock	0.44
Birch, yellow	0.66	Pine, jack	0.46
Chestnut	0.46	Pine, Norway	0.51
Elm, white	0.54	Pine, longleaf	0.64
Maple, sugar	0.66	Spruce, white	0.43
Oak, white	0.71	Tamarack	0.56

Woods of the highest specific gravity are found in tropical and subtropical regions. The black ironwood (*Rhamnidium ferreum*) of Florida has the highest specific gravity, namely, 1.302, of any wood native to the United States.

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[1] E. RICHTER, *Wochbl. Papierfabr.*, **46** (1915), 1529–1533.

[2] H. DE MOSENTHAL, *J. Soc. Chem. Ind.*, **26** (1907), 445.

From 40 to 80 per cent of the total volume of wood is occupied by air. Since the density of wood substance is approximately 1.54, it may be calculated that 100 parts of wood having a specific gravity of 0.40 can take up 185 parts of water. Maumené[1] tested 32 species of woods and found that the highest absorption was shown by chestnut, 100 parts of which took up 174.86 parts of water.

Refractive Index.—Celluloses obtained by denitration of the nitrates of wood cellulose, ramie, flax, and cotton had about the same refractive index, namely $n_D = 1.5310$.[2]

Double Refraction.—According to Tunmann,[3] lignified membranes are more strongly refractive than pure cellulose membranes. Under polarized light, dense walls show a dark cross. On ultramicroscopic examination, they show an approximately parallel series of large, strongly luminous micellæ between which are optically empty spaces. Remec[4] states that lignin has no influence on the specific double refraction of plant fibers.

It has been assumed until recently that the double refraction of cellulose was due to the presence of anisitropic crystals. According to Harrison,[5] double refraction is due to internal stresses running parallel to the axis of the fiber. It disappears when the strain is relieved by swelling the fiber in cuprammonium solution except in those bands unaffected by the reagent.

It has been found by Ambronn[6] that when fine strands of substances are imbedded parallel to each other so as to form a grating in a medium having a different refraction, the system behaves as a uniaxial positive crystal. If the medium has a similar refractive index, this effect disappears while true double refraction persists. Under the latter conditions, cellulose fibers obtained by the denitration of collodion show a strong double refraction which clearly indicates crystalline anisitropy. Katz[7] states that the double refraction of cellulose is most simply explained on the assumption that the fibers are built up of micellæ or minute crystals.

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[1] E. J. Maumené, *Compt. rend.*, **87** (1878), 943–946.

[2] H. de Mosenthal, *J. Soc. Chem. Ind.*, **26** (1907), 447.

[3] O. Tunmann, "Pflanzenmikrochemie," (1913), p. 593.

[4] E. Remec, *Akad. Wiss. Wien*, **110**, I (1901), 387.

[5] W. Harrison, *Proc. Roy. Soc.*, **94A** (1908), 460–469.

[6] H. Ambronn, *Kolloid-Z.*, **18** (1916), 90–97, 273–281.

[7] J. R. Katz, *Kolloidchem. Beihefte*, **9** (1917), 160.

Fluorescence.—In 1893, Hartley[1] found that blotting paper was strongy fluorescent and capable of rendering visible the whole of the ultra-violet spectrum as far as wave length 2000. This fluorescence lacks distinct color.

The subject has been extensively investigated by Lewis.[2] Mechanical pulp is devoid of fluorescent properties and cellulose nitrate nearly so. Normal cellulose from all sources gives a nearly uniform spectrum. Mercerized cellulose, viscose, parchment, and paper from well-beaten pulps show a characteristic and distinct effect at wave length 2750. Each modified cellulose has a characteristic curve. It appears that constituent groups within the cellulose molecule affect the fluorescent properties, as indicated by distortion of the curve, so that it may eventually be possible to detect differences in constitution in this way.

Specific Heat.—Fleury[3] obtained 0.366 for the specific heat of dry cellulose and 0.41 for cellulose containing 7 per cent of water. The following values were obtained by Dietz:[4]

	Specific Heat
Artificial silk	0.324
Filter paper	0.319
Sulphite pulp	0.319
Soda pulp	0.323
Straw pulp	0.325
Mechanical pulp, pine	0.327
Cotton	0.319

There evidently is little difference between the specific heats of cellulose and lignocellulose.

Dunlap[5] determined the specific heats of a large number of woods. The samples were dried at 105°. There was little variation between species. The portion of the tree from which the samples were taken and the locality in which the trees grew were without effect. The mean value was 0.327. The specific heat is greatly influenced by temperature and is represented by the equation

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[1] W. N. Hartley, *J. Chem. Soc.*, **63** (1893), 253.

[2] S. J. Lewis, *J. Soc. Dyers Colourists*, **34** (1918), 167–172; **37** (1921), 201–204; **38** (1922), 68–76, 99–108.

[3] G. Fleury, *Compt. rend.*, **130** (1900), 437.

[4] O. Dietz, *Wochbl. Papierfabr.*, **43** (1912), 3119–3123.

[5] F. Dunlap, "The Specific Heat of Wood," *Forest Service Bull.*, **110** (1912), 28 pp.

$$\text{Specific heat} = 0.266 + 0.00116t,$$

in which 0.266 represents the specific heat at 0°. Padoa[1] gives the specific heat of cellulose as 0.347 between 0 and 80°.

Thermal Conductivity.—The thermal conductivity of cellulose and wood fibers is much greater than that of air, so that the greater the density of the wood the poorer is its insulating property. The following values were obtained by van Dusen:[2]

Material	Remarks	Thermal conductivity		Density	
		$K \times 10$	k	D	d
Balsa wood	Very light; across grain	10.7	7.5	0.113	7.1
Ceiba wood	Across grain	11.3	7.9	0.113	7.1
Balsa wood	Across grain	11.9	8.3	0.118	7.4
Sawdust	Various	14.0	9.7	0.190	12.0
Planer shavings	Various	14.0	10.0	0.140	8.8
Balsa wood	Heavy	20.0	14.0	0.33	20.0
Cypress	Across grain	23.0	16.0	0.46	29.0
White pine	Across grain	27.0	19.0	0.50	32.0
Mahogany	Across grain	31.0	22.0	0.55	34.0
Virginia pine	Across grain	33.0	23.0	0.55	34.0
Oak	Across grain	35.0	24.0	0.61	38.0
Maple	Across grain	38.0	27.0	0.71	44.0

K = thermal conductivity in cal. sec.$^{-1}$ cm.$^{-1}$ deg.$^{-1}$.
k = thermal conductivity in B.t.u. per 24 hours, per square foot, per degree Fahrenheit, per inch of thickness.
$k = 69{,}700\ K$.
D = density in grams per cubic centimeter.
d = density in pounds per cubic foot.
$d = 62.5D$.

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[1] M. Padoa, *Atti accad. Lincei, rend.*, **29** (1920), 201.

[2] M. S. van Dusen, *Trans. Am. Soc. Heating, Ventilating Eng.*, **26** (1920), 406; *cf.* C. Niven and A. E. M. Geddes, *Proc. Roy. Soc.*, **87A** (1912), 535–539; T. S. Taylor, *Mech. Eng.*, **42** (1920), 8–10.

The conductivities of the woods measured fall roughly on a straight line when plotted against density.

Railway ties 6 by 8 inches in cross-section required steaming at 20 pounds pressure for an average period of 4 hours and 20 minutes before the center reached a temperature of 100°.[1]

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[1] G. M. Hunt, *Proc. Am. Wood-Preservers' Assoc.*, **11** (1915), 85–99.

CHAPTER II

THE COMPOSITION OF WOOD

The development of our knowledge of the composition of plant tissues and of the fundamentals of present analytical methods is due preeminently to the earlier French investigators.

History.—Payen[1] observed that the carbon content of oak, beech, and poplar was reduced by treatment with alkali. The "thickening substance" deposited in the lignified cells differed from the membrane proper and was attacked by alkalis and nitric acid. Rasped wood was treated with 20 times its weight of concentrated nitric acid, allowed to stand 30 hours, and washed with sodium hydroxide. There remained a residue of *cellulose,* isomeric with starch. Analysis showed:[2]

	Per Cent
C	43.85
H	5.86
O	50.28

Wood was recognized as consisting of two principal substances, cellulose and "true ligneous matter." The "*matière incrustante*" had a higher carbon content[3] than the cellulose, analysis showing:

	Per Cent
C	53.76
H	6.00
O	40.20

The existence of incrusting material was denied by Fremy,[4] who thought that the cell walls contained several fiber substances differing from one another in their solubility in various chemicals. The starch-free cells of roots and fruits were treated with cuprammonium solution to dissolve the cellulose. The green-colored inner membrane remaining consisted of a salt of pectic acid, which was made soluble by treatment with hydrochloric acid followed by caustic potash. Fungi and the pith of certain trees behaved differently under the same treatment, so that he assumed the existence of various celluloses. This, in turn, was denied by Payen,[1] who attributed the variable properties of cellulose from different sources to the difference in degree of adhesion between the cellulose and the compounds with which it was associated.

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[1] A. Payen, *Compt. rend.,* **7** (1838), 1052–1056.

[2] A. Payen, *Compt. rend.,* **7** (1838), 1125; **8** (1839), 52.

[3] A. Payen, *Compt. rend.,* **8** (1839), 169.

[4] E. Fremy, *Compt. rend.,* **48** (1859), 202–208.

It was then shown by Fremy[2] that density played but a small part with respect to solubility in cuprammonium solution, since vegetable ivory dissolved rapidly while wood fibers did not. As proof of the existence of definite isomeric substances, he showed that rice paper, insoluble in its original condition, became soluble in cuprammonium solution after treatment with dilute mineral acids or caustic alkalis. In this way cellulose could be extracted from paper but not from fungi. Payen[3] maintained his original position that the cellulose in woody plants did not differ essentially from that of cotton and other textile fibers; when sufficiently free from incrusting materials, all dissolved in Schweizer's reagent.

Pelouze[4] showed that cellulose precipitated from cuprammonium solution was then soluble in hydrochloric acid of a concentration in which ordinary cellulose would not dissolve; that concentrated hydrochloric acid would dissolve cellulose, water precipitating it in a form like that from a cuprammonium solution. Payen[5] later recognized the existence of isomeric celluloses, but maintained that it had not yet been shown that the soluble cellulose could be distinguished chemically from that in plants; the latter could be rendered soluble in cuprammonium solution, by treating the tissues with glacial acetic acid, without destroying the structure of the cells.

In a paper devoted specifically to the chemical composition of wood, Fremy[6] rejected the idea that wood consists of cellulose impregnated with foreign substances. The term "cellulose" was reserved for substances like cotton and vegetable ivory which were directly soluble in cuprammonium solution. Wood fibers were first treated with dilute potassium hydroxide to remove tannins, albumin, and pectic substances, followed by hydrochloric acid of varying strength, fuming acid being finally used; the fibers were then soluble in cuprammonium solution. He finally treated them with concentrated sulphuric acid to remove the "utricular or fibrous" parts unaffected by the previous treatments. In this way were isolated *vasculose*, *paracellulose*, and *fibrose*.

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[1] A. Payen, *Compt. rend.*, **48** (1859), 210–221.

[2] E. Fremy, *Compt. rend.*, **48** (1859), 275–279.

[3] A. Payen, *Compt. rend.*, **48** (1859), 319–325.

[4] J. Pelouze, *Compt. rend.*, **48** (1859), 210, 327.

[5] A. Payen, *Compt. rend.*, **48** (1859), 328, 358.

[6] E. Fremy, *Compt. rend.*, **48** (1859), 862–868.

Vasculose was the substance of which the vessels and tracheids were composed. It was insoluble in acids and cuprammonium solution but dissolved in boiling concentrated potassium hydroxide. The medullary rays contained *paracellulose;* it was insoluble in cuprammonium solution but became soluble after treatment with acids and alkalis, or under the influence of heat and moisture. Pieces of oak and fir after treatment with concentrated potassium hydroxide gave a white fibrous residue like paper pulp, called *fibrose*. His description of the latter is somewhat ambiguous. It was insoluble in cuprammonium solution in which cellulose dissolves at once and in the alkaline solution which dissolved the medullary rays. *Fibrose* was to be distinguished from cellulose in that when water was added to its solution in concentrated suphuric acid a thick jelly precipitated; cellulose under the same conditions gave dextrins not precipitable by water.

In a later paper the opinions of Fremy[1] as to the composition of wood were modified to accord more closely with those of Payen. Analysis of wood comprised determination of "ligneous cuticle" or "cuticular substance," the "incrusting substance" of Payen, and true cellulose. The "ligneous cuticle" represented the residue remaining after treatment with sulphuric acid ($H_2SO_4 + 2H_2O$), and washing with water and alkali. Cellulose was determined by suspending the wood in chlorine water followed by washing with potassium hydroxide. The true incrusting substance was determined by difference. Oak wood had the following composition:

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[1] E. Fremy and A. Terreil, *Compt. rend.*, **66** (1868), 456–460; *Bull. soc. chim.*, **9** (1868), 437–441.

	PER CENT
Ligneous cuticle	20
Cellulose	40
Incrusting matter	40

The incrusting matter consisted of 10 per cent of substances soluble in water, 15 per cent soluble in alkali, and 15 per cent of acid bodies, soluble in alkali, formed by action of the chlorine. The ligneous cuticle (lignin) contained more carbon than cellulose.

The substances present in vegetable tissues are subsequently[1] stated to be: (1) cellulose bodies; (2) vasculose; (3) cutose; (4) pectose; (5) calcium pectate; (6) nitrogenous substances; and (7) mineral substances. The cellulose bodies, cellulose, paracellulose, and metacellulose, are distinguished from one another by their reaction to cuprammonium solution; cellulose dissolves immediately, paracellulose only after the action of acids, while metacellulose, which is found principally in fungi and lichens, is insoluble even after the action of acids. Vasculose cements the cells together and forms a large part of the vessels and tracheids; it contains more carbon and less hydrogen than cellulose, is rapidly attacked by oxidizing agents, and is insoluble in cuprammonium solution and 72 per cent sulphuric acid. Cutose, the fine membrane covering leaves and the green parts of plants, is soluble in alkali. Pectose after treatment with hydrochloric acid becomes soluble in water, from which it can be precipitated with alcohol.

Fremy and Urbain[2] were of the opinion that a hard wood contained more lignin (vasculose) than a soft wood. Poplar contained 18 per cent of lignin and ironwood (*bois de fer*) 40 per cent. It is now known that there is no relation between hardness or specific gravity and lignin content. Vasculose was isolated by treating the wood with neutral solvents, dilute alkalis and acids, and exhausting with cuprammonium solution. The light-yellow residue had the appearance of the original tissue. Atmospheric oxygen in time changed it into a resinous mass soluble in alkali. Through this modification of vasculose was explained the changes which wood undergoes in contact with the air.

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[1] E. FREMY, *Compt. rend.*, **83** (1876), 1136–1141; **93** (1881), 926–931.

[2] E. FREMY and URBAIN, *Compt. rend.*, **94** (1882), 108.

The compound celluloses have been classified as follows:

1. Lignocelluloses contain lignin; wood, straw, jute, etc.
2. Pectocelluloses and mucocelluloses contain pectic and mucilaginous or gummy substances; the former are represented by hemp, flax, and ramie, and the latter by algæ and various fruits and tubers.
3. Adipocelluloses and cutocelluloses contain waxy and fatty compounds. Cork, an adipocellulose, contains among other substances phellonic and suberic acids. The epidermis of the leaves and twigs of phanerogams contains cutin or cutose; on saponification with alkalis two principal fatty acids, stearocutic,[1] $C_{28}H_{48}O_4$, and oleocutic, $C_{15}H_{20}O_4$, are obtained.

The above classification based on the researches of Fremy has the merit of convenience, but in a strict sense it is not accurate. Many fibrous materials would fall into two or more classes. Carried to a logical conclusion no simple cellulose exists in nature, since even raw cotton contains small amounts of cutin and pectin. The non-cellulose compounds are associated with cellulose in very variable amounts and there is little evidence of a chemical union with the cellulose.

It has been a much disputed point whether in the wood the lignin is chemically combined with the cellulose, admixed, or adsorbed. Sachsse[2] compared wood with an alloy; it consisted of cellulose particles intimately incrusted by other substances originating from it or the cell contents. Von Baumhauer[3] working with fruit pits supported the view of Payen that the non-cellulose constituents were mixed in different proportions with cellulose, though in peach stones the incrusting material was so intimately associated with the cellulose that it could not be removed with strong potassium hydroxide. The incrustation hypothesis was also favored by Schulze.[4]

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[1] E. Fremy and Urbain, *Compt. rend.*, **100** (1885), 19–24.

[2] R. Sachsse, "Die Chemie und Physiologie der Farbstoffe, Kohlenhydrate und Proteinsubstanzen" (1877), p. 146.

[3] E. H. von Baumhauer, *J. prakt. Chem.*, **32** (1844), 210.

[4] F. Schulze, *Chem. Centr.*, **28** (1857), 321.

Kabsch[1] thought that lignin was a decomposition product of the cellulose and remained combined with it. Later Erdmann[2] held Payen's incrusting material to be a definite compound chemically combined with the cellulose. The wood of the silver fir (*Pinus abies L.*) after treatment with hot dilute acetic acid, hot water, alcohol, and ether was called "glycolignose" and assigned the formula $C_{30}H_{46}O_{21}$. The latter on hydrolysis gave sugar and 60 to 65 per cent of "lignose," $C_{18}H_{26}O_{11}$. Lignose on heating with dilute nitric acid gave cellulose. Glycolignose was looked upon as a chemical entity, owing to the constancy of its composition and the inability of cuprammonium solution to remove more than traces of cellulose. Lignin was so difficult to remove from cellulose that Hoppe-Seyler[3] and others[4] thought that the two must be combined as an ester or ether.

The chemical combination theory was early championed by Cross and Bevan.[5] Jute was assigned the formula $(C_6H_{10}O_5)_3$.-$C_6H_6O_3$ and considered a definite compound since the fiber was attacked by hot alkalis and non-oxidizing mineral acids with loss of weight "but without producing any essential change in the insoluble residue"; it is not resolved by cuprammonium solution; and lignocellulose can be nitrated as such to give a definite tetranitrate. Mühlhäuser[6] likewise obtained a definite jute nitrate behaving as a homogeneous substance. Treatment with alkalis left residues containing practically the same percentage of nitrogen as the original material.

It is stated by Cross and Bevan[7] that, while the lignocelluloses are incompletely dissolved by such solvents as concentrated zinc chloride and cuprammonium solutions, and are incompletely precipitated from these solutions, there is no essential difference in reactions between the soluble and insoluble portions; they have the empirical composition of the original fiber. In another work the question of a chemical union is left open.[1] The writer, employing cuprammonium solution[2] and the thiocarbonate reaction,[3] has found in the case of wood a decided difference in composition between the soluble and insoluble portions; with the angiosperms especially the residues are much higher in lignin than the soluble portion.

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[1] W. Kabsch, *Jahrb. wiss. Botanik*, **3** (1863), 369.

[2] J. Erdmann, *Ann. Suppl.*, **5** (1867), 223–232.

[3] F. Hoppe-Seyler, *Z. physiol. Chem.*, **13** (1889), 84.

[4] G. Lange, *Z. physiol. Chem.*, **14** (1890), 19; F. Czapek, *Ibid.*, **27** (1899), 165; V. Grafe, *Monatsh.*, **25** (1904), 987.

[5] C. F. Cross and E. J. Bevan, *J. Chem. Soc.*, **55** (1889), 199; *cf. Ber.*, **24** (1891), 1772; **26** (1893), 2520.

[6] O. Mühlhäuser, *Dinglers polytech. J.*, **283** (1892), 88, 137.

[7] C. F. Cross and E. J. Bevan, "Cellulose" (1916), p. 114.

When wood is treated with 72 per cent sulphuric acid the insoluble residue shows under the microscope the identical structure of the original material; for this reason König and Rump[4] maintain that it is erroneous to assume a chemical union between the cellulose and associated compounds, and that the present classification of the compound celluloses can no longer be supported. This argument against chemical union has little force when the behavior of some of the cellulose esters is considered; cellulose nitrate, *e.g.*, in the form of threads and tissues can be denitrated to give a cellulose skeleton identical with the original in physical form.

According to von Euler,[5] lignin is chemically combined with carbohydrates in wood, the union being that of a tannin glucoside. Karrer and Widmer[6] believe that cellulose and lignin are not chemically combined, since wood dissolves in acetylbromide to give a separable mixture of the decomposition products of cellulose and lignin. This argument is also without weight as the reaction is mainly hydrolytic; it will not take place in the absence of moisture or when the acetylbromide is free from hydrogen bromide.[7]

The formation of wood has been studied by Wislicenus and Kleinstück[8] from a colloidal viewpoint. The cellulose hydrogels on coagulation form the cell tissues, which are thickened by adsorption from the sap of such substances as lignin, which is a variable mixture. Esterification and other chemical processes may take place, but they play a minor part.

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[1] C. F. Cross and E. J. Bevan, "Researches," III (1905–1910), p. 109.

[2] A. W. Schorger, *J. Ind. Eng. Chem.*, **16** (1924), 143.

[3] Unpublished results.

[4] J. König and E. Rump, "Chemie und Struktur der Pflanzen-Zellmembran," Berlin (1914), p. 85.

[5] A. C. von Euler, *Cellulosechemie*, **3** (1922), 4.

[6] P. Karrer and F. Widmer, *Helvetica Chim. Acta*, **4** (1921), 700.

[7] L. Zechmeister, *Ber.*, **56** (1923), 573.

[8] H. Wislicenus and M. Kleinstück, *Z. Chem. Ind. Kolloide*, **6** (1910), 17–23, 87–94.

Röntgen-ray spectrograms of jute and linden wood powder gave patterns differing from cotton cellulose only within the limit of experimental error; but whether lignin is adsorbed or chemically combined can only be determined by more extensive investigations.[1]

Constituents of Wood.—The major constituents of all woods are lignin, cellulose, and hemicelluloses; the latter comprise only those carbohydrates which are substantially insoluble in water. Ash, starch, and protein are always present in small amounts. The inclusion of pectin as a primary minor constituent is problematical. Wood contains variable amounts of secondary constituents, secreted from the living cells, which do not properly form a part of the wood complex. The major constituents are treated in separate chapters.

Elementary Composition of Wood.—In 1844, Chevandier[2] subjected wood from the trunk and branches of various species of trees to elementary analysis. The two forms of wood gave very similar results, the carbon content of the branches being somewhat the higher. The trunk wood had the following composition:

	Beech	Oak	Birch	Aspen	Willow
C................	49.89	50.64	50.61	50.31	51.75
H................	6.07	6.03	6.23	6.32	6.19
O................	43.11	42.05	42.04	42.39	41.08
N................	0.93	1.28	1.12	0.98	0.98
Ash..............	1.24	2.05	0.78	1.86	3.67

The elementary percentages are based on the ash-free wood. The results for nitrogen and ash are too high.

Analyses by Gottlieb[3] are given below. His values for nitrogen and ash are normal.

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[1] R. O. Herzog and W. Jancke, *Ber.*, **53** (1920), 2163.

[2] E. Chevandier, *Ann. chim. phys.*, [3] **10** (1844), 143.

[3] E. Gottlieb, *J. prakt. Chem.*, **136** (1883), 392.

Species	C	H	O and H		Ash
Oak (*Quercus pedunculata*)	50.16	6.02	43.45		0.37
Ash (*Fraxinus excelsior*)	49.18	6.27	43.98		0.57
Hornbeam (*Carpinus betulus*)	48.99	6.20	43.31		0.50
Beech (*Fagus silvatica*):					
60 years old	49.14	6.16	44.07	0.09	0.54
130 years old	49.03	6.06	44.36	0.11	0.44
100 years old	48.87	6.14	44.29	0.06	0.64
Birch (*Betula alba*)	48.88	6.06	44.67	0.10	0.29
Pine (*Pinus silvestris*)	50.36	5.92	43.39	0.05	0.28
Spruce (*Pinus abies*)	50.31	6.20	43.08	0.04	0.37

Daube[1] attempted to distinguish between heartwood and sapwood by ultimate analysis. In pine only did the heartwood contain more carbon than the sapwood, and this was attributed to the presence of resin.

	Age in years									
	103		104		75		125		180	
	Larch		Pine		Spruce		Oak		Beech	
	Sapwood	Heartwood	Sapwood	Heartwood	Sapwood	Heartwood	Sapwood	Heartwood	Sapwood	Heartwood
C	49.57	49.86	50.18	54.38	50.03	49.55	49.15	50.28	48.92	49.06
H	5.85	5.91	6.08	6.31	6.05	6.18	5.84	5.62	5.86	5.91
N	0.17	0.12	0.17	0.56	0.19	0.18	0.35	0.28	0.24	0.22
O	44.19	43.99	43.38	39.00	43.47	43.89	44.24	43.66	44.51	44.41
Ash	0.22	0.12	0.19	0.15	0.26	0.20	0.42	0.16	0.47	0.40

The leaching of chestnut wood to remove the tannins had little effect on the ultimate analysis, as shown by the following:[2]

	C	H	O	N	S	Ash
Chestnut wood, normal	50.28	5.58	43.21	0.10	0.03	0.80
Chestnut wood, leached	50.09	5.65	43.33	0.10	0.02	0.81

It will be observed that wood contains approximately 50 per cent of carbon, 6 per cent of hydrogen, and 44 per cent of oxygen. Ultimate analysis shows no distinction between hardwoods and softwoods, or between sapwood and heartwood.

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[1] W. Daube, *Forstliche Blätter*, **20** (1883), 177–192.

[2] H. S. Sherman and C. G. Amend, *School Mines Quart.*, **33** (1911), 30.

Analytical Composition of Wood.—Within recent years fairly complete analyses showing the composition of wood have been made (Tables 2 to 4). In general, hardwoods contain more pentosans, acetyl and methoxyl groups, and less lignin and pentosan-free cellulose than the softwoods (gymnosperms). Incense cedar is exceptional in having a methoxyl value comparable to that of the hardwoods, but its lignin content is very high (37.7 per cent). Mesquite has a lignin content comparable with that of the softwoods, but the cellulose content is very low. Balsa, noted for its lightness. does not differ in composition from the average hardwood.

The hardwoods contain more hemicellulose than the softwoods, the principal one being xylan. Mannan and galactan may be present in softwoods in considerable amounts, while only traces appear in hardwoods. König and Becker[1] (Tables 1 and 4) determined hemicellulose by heating the wood with 0.4 per cent sulphuric acid at arbitrary pressures: 2.5 atmospheres for fir, 3.5 for pine, 2.25 for birch, and 1.0 for beech. Galactose was determined by oxidation to mucic acid, glucose by oxidation to saccharic acid, and mannose as the phenylhydrazone. Fructose was not found.

TABLE 1.—SUGARS IN HEMICELLULOSES

Sugar	Fir, per cent	Pine, per cent	Birch, per cent	Beech, per cent
Pentose (xylose)	26.0	24.8	61.1	73.9
Glucose	23.4	21.4	14.4	20.1
Galactose	3.4	4.2	3.5	0.1
Mannose	24.6	43.4	7.1	3.3

Dore[2] has laudably attempted to account for all of the major constituents of wood. The contention is made that by the methods employed no constituents of importance are overlooked, and the overlapping of constituents is avoided. Undue weight may be placed on a summation approaching 100 per cent. Less information on the composition of the woods is available

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[1] J. König and E. Becker, *Z. angew. Chem.*, **32** (1919), 155.

[2] W. H. Dore, *J. Ind. Eng. Chem.*, **12** (1920), 476, 984.

TABLE 2.—ANALYSES OF AMERICAN WOODS

(Results in percentages of oven-dry (105°C.) samples)

Species	Sample	Moisture	Ash	Solubility in				Acetic acid	Methoxyl	Pentosan	Methylpentosan	Cellulose	Lignin	In cellulose				
				Cold water	Hot water	Ether	1 per cent NaOH							Pentosan	Methylpentosan	α-Cellulose	β-Cellulose	γ-Cellulose
Western yellow pine[1] (*Pinus ponderosa*)	141	5.32	0.43	5.58	5.67	9.63	22.08	0.92	4.55	8.06	1.68	56.22	26.75	9.50	2.13	69.18	.....	30.82
	142	8.28	0.42	2.97	3.40	6.52	16.58	1.24	4.02	9.96	1.24	57.72	25.85	8.97	1.97	66.17	5.52	28.31
	143	6.89	0.55	4.62	6.33	9.45	23.16	1.03	4.51	5.88	1.81	58.88	26.29	4.20	1.90	57.65	6.54	35.80
	144	5.19	0.44	3.17	4.89	6.48	19.37	1.18	4.87	5.52	1.77	56.82	27.72	4.63	1.90	55.40	19.02	25.58
	Mean	6.42	0.46	4.09	5.05	8.52	20.30	1.09	4.49	7.35	1.62	57.41	26.65	6.82	1.98	62.10	10.56	30.13
Yellow cedar[1] (*Chamæcyparis nootkatensis*)	161	3.54	0.33	1.66	2.89	2.67	13.80	1.66	5.42	8.86	3.97	51.45	33.21	8.60	2.03	62.88	11.10	26.02
	162	5.19	0.35	3.03	3.46	3.34	14.49	1.62	5.60	8.52	3.57	54.04	31.27	8.09	1.91	62.96	10.99	26.05
	163	4.87	0.62	2.47	2.86	2.08	12.69	1.55	5.05	6.72	2.97	54.78	30.43	6.65	1.65	59.37	11.64	28.97
	164	5.91	....	2.74	3.23	2.11	12.67	1.54	4.92	7.37	3.17	55.17	30.27	5.86	1.54	65.52	10.51	23.97
	Mean	4.89	0.43	2.47	3.11	2.55	13.41	1.59	5.25	7.87	3.42	53.86	31.32	7.30	1.78	62.68	11.06	26.25
Incense cedar[1] (*Libocedrus decurrens*)	165	5.32	0.38	3.09	4.87	3.33	17.37	0.96	6.34	11.07	1.20	39.94	38.14	9.53	2.13	48.47	15.42	36.11
	166	4.63	0.27	2.53	3.62	4.69	13.81	1.04	6.29	9.99	1.60	44.10	37.73	7.90	1.71	41.42	12.77	45.81
	167	5.42	0.38	5.31	7.64	4.90	21.89	0.73	6.09	10.70	1.26	40.76	37.17	9.83	2.13	50.90	6.82	42.28
	Mean	5.12	0.34	3.64	5.38	4.31	17.69	0.91	6.24	10.65	1.35	41.60	37.68	9.08	1.99	46.92	11.67	41.06
Redwood[1] (heartwood) (*Sequoia sempervirens*)	168	9.64	0.22	7.31	9.77	1.00	20.06	1.03	5.27	7.93	2.77	48.67	34.18	7.40	2.09	78.81	2.95	18.24
	168	9.71	0.20	7.40	9.94	1.14	19.94	1.13	5.16	7.67	2.74	48.23	34.25					
	Mean	9.68	0.21	7.36	9.86	1.07	20.00	1.08	5.21	7.80	2.75	48.45	34.21	7.40	2.09	78.81	2.95	18.24
Western white pine[2] (*Pinus monticola*)	1	6.18	0.21	2.60	3.35	4.00	13.97	1.21	4.38	6.75	3.41	58.53	27.22	4.47	1.59	70.58	18.16	11.26
	2	7.68	0.20	1.73	2.57	4.42	12.70	0.94	4.59	7.19	3.25	62.29	24.15	5.68	2.97	64.34	10.69	24.97
	3	7.00	0.18	3.92	7.25	3.98	15.92	1.37	4.86	6.48	3.33	59.40	27.55	5.19	1.68	74.29	9.17	16.54
	4	7.15	0.19	4.40	4.78	4.63	16.51	1.09	4.41	7.46	2.90	58.61	26.82	5.96	1.56	49.27	27.27	23.46
	Mean	7.00	0.20	3.16	4.49	4.26	14.78	1.03	4.56	6.97	3.22	59.71	26.44	5.33	1.95	64.61	16.32	19.06
Longleaf pine[3] (*Pinus palustris*)	11	....	0.40	7.75	8.20	6.70	24.62	0.70	5.00	7.33	3.48	55.33	.....	8.38	1.26			
	12	....	0.34	5.60	6.03	6.70	21.07	0.93	4.90	7.52	3.29	57.53	.....	7.19	1.39			
	13	....	0.35	5.40	6.78	2.65	18.89	0.62	5.26	7.57	3.87	61.41	.....	7.39	1.03			
	20	....	0.38	6.05	7.57	9.23	24.87	0.79	5.03	7.43	3.67	59.67	.....	7.90	0.96			
	Mean	....	0.37	6.20	7.15	6.32	22.36	0.76	5.05	7.46	3.60	58.48	.....	7.71	1.16			

Douglas fir³ (*Pseudotsuga taxifolia*)	1	....	0.40	3.79	6.62	0.94	15.82	0.93	4.81	6.03	4.24	61.97	.....	5.56	1.26			
	2	....	0.37	3.16	6.07	1.00	16.76	1.01	5.17	6.30	4.64	57.00						
	3	....	0.35	2.94	6.36	1.11	15.12	1.13	4.88	6.00	4.38	63.08						
	5	....	0.38	4.25	6.96	1.02	16.72	1.07	4.92	5.73	4.38	63.82	.....	5.12	1.15			
	Mean	....	0.38	3.54	6.50	1.02	16.11	1.04	4.95	6.02	4.41	61.47	.....	5.34	1.20			
Western larch³ (*Larix occidentalis*)	1	....	0.21	10.45	12.57	0.72	22.07	0.61	5.08	11.15	2.47	58.25	.....	9.12	1.40			
	2	....	0.32	11.00	12.40	0.74	21.93	0.91	4.91	11.04	2.83	58.71	.....	8.41	1.22			
	3	....	0.22	8.16	10.08	0.93	19.44	0.76	5.08	10.22	3.14	60.91	.....	8.67	1.24			
	4	....	0.16	12.83	15.30	0.83	25.11	0.55	5.05	10.78	2.80	53.31	.....	9.55	0.90			
	Mean	....	0.23	10.61	12.59	0.81	22.14	0.71	5.03	10.80	2.81	57.80	.....	8.94	1.19			
White spruce³ (*Picea canadensis*)	1	....	0.33	1.28	1.88	1.95	11.33	1.58	5.31	10.78	3.08	62.61	.....	10.26	0.83			
	2	....	0.29	0.92	2.28	0.90	11.58	1.57	5.26	10.31	3.52	63.29	.....	9.29	0.68			
	3	....	0.30	1.45	2.52	0.97	12.75	1.49	5.29	10.04	3.95	60.43						
	4	....	0.32	0.82	1.88	1.63	10.63	1.73	5.32	10.42	3.64	61.09	.....	9.33	0.66			
	Mean	....	0.31	1.12	2.14	1.36	11.57	1.59	5.30	10.39	3.55	61.85	.....	9.63	0.72			
Tanbark oak¹ (*Quercus densiflora*)	151	4.10	0.78	4.14	5.25	0.74	22.59	5.70	5.34	20.02	....	59.40	23.29	23.22	....	55.50	18.81	25.64
	152	3.95	0.81	4.32	6.15	0.73	25.33	5.70	6.19	20.00	....	56.50	26.07	25.46	....	55.91	2.95	41.14
	153	3.26	0.82	4.22	5.92	0.80	23.91	4.40	5.35	19.13	....	57.27	25.20	20.30	....	58.15	22.62	19.23
	154	3.36	0.91	3.72	5.08	0.98	22.93	5.13	6.09	19.22	....	58.95	24.86	22.32	....	57.82	18.27	24.21
	Mean	3.66	0.83	4.10	5.60	0.80	23.96	5.23	5.74	19.59	....	58.03	24.85	22.82	....	56.77	19.92	23.03
Mesquite¹ (*Prosopis juliflora*)	171	4.53	0.57	12.55	15.27	2.20	28.72	1.53	5.68	14.04	0.59	44.79	30.27	17.99	1.07	76.00	1.73	22.27
	172	6.10	0.58	13.50	15.77	....	30.08	1.70	5.69	13.99	0.69	45.28	30.13	17.99	1.21	76.71	2.56	20.73
	173	6.15	0.49	12.68	15.56	2.33	29.60	2.53	5.29	13.85	1.18	45.87	31.28	17.57	....	76.40	2.06	21.54
	174	5.20	0.50	11.74	13.77	2.37	25.69	2.37	5.66	13.95	0.34	45.97	30.22	17.44	0.96	76.83	3.04	20.13
	Mean	5.49	0.54	12.62	15.09	2.30	28.52	2.03	5.55	13.96	0.70	45.48	30.47	17.75	0.81	76.48	2.35	21.17
Balsa¹ (*Ochroma lagopus*)	175	5.50	2.15	1.85	2.84	1.27	20.37	5.75	5.71	17.51	0.88	54.04	26.52	19.99	1.35	75.64	0.27	24.08
	175	6.44	2.09	1.68	2.74	1.19	20.36	5.85	5.65	17.79	0.83	54.24	26.47					
	Mean	6.47	2.12	1.77	2.79	1.23	20.37	5.80	5.68	17.65	0.86	54.15	26.50	19.99	1.35	75.64	0.27	24.08
Hickory (shellbark)¹ (*Hicoria ovata*)	177	9.60	0.65	4.71	5.41	0.65	18.65	2.60	5.61	18.58	0.92	55.60	23.83	21.33	1.64	75.27	2.64	22.09
	178	7.39	0.74	4.86	5.73	0.62	19.44	2.42	5.65	19.06	0.67	56.85	23.04	22.45	1.19	77.38	3.01	18.61
	Mean	8.49	0.69	4.78	5.57	0.63	19.04	2.51	5.63	18.82	0.80	56.22	23.44	21.89	1.41	76.32	2.82	20.35
Eucalyptus² (*Eucalyptus globulus*)	1	6.99	0.23	2.65	4.41	0.54	16.57	2.31	7.11	21.41	1.97	59.67	24.04	20.35	3.92	67.85	2.11	31.04
	2	6.55	0.20	4.93	6.96	0.52	18.42	1.97	6.37	20.66	2.14	58.53	25.24	21.62	2.44	69.75	0.00	31.25
	3	6.87	0.27	5.31	8.26	0.60	17.90	1.51	6.87	17.90	2.74	56.45	25.07	20.10	2.24	68.99	0.00	31.01
	4	5.90	0.24	5.79	8.27	0.59	21.40	1.62	6.56	20.39	2.48	55.83	26.74	21.76	1.26			
	Mean	6.58	0.24	4.67	6.98	0.56	18.57	1.85	6.73	20.09	2.33	57.62	25.07	20.96	2.46	68.86	0.70	31.10

TABLE 2. — ANALYSES OF AMERICAN WOODS. — (*Continued*)

Species	Sample	Moisture	Ash	Solubility in				Acetic acid	Methoxyl	Pentosan	Methylpentosan	Cellulose	Lignin	In cellulose				
				Cold water	Hot water	Ether	1 per cent NaOH							Pentosan	Methylpentosan	α-Cellulose	β-Cellulose	γ-Cellulose
Basswood[3] (*Tilia americana*)..........	1	....	0.80	2.04	3.84	1.50	23.43	5.78	6.23	19.82	3.72	62.92	.....	24.48	1.19			
	2	....	0.74	1.63	2.94	1.14	21.61	6.14	6.05	19.54	3.85	62.41	.....	23.54	1.46			
	3	....	0.96	3.14	5.66	3.59	26.93	5.46	6.11	20.37	3.68	54.66	.....	26.61	1.62			
	4	....	0.94	1.23	3.22	0.89	21.46	5.41	5.91	19.14	4.16	63.13	.....	21.89	1.45			
	5	....	0.85	2.55	4.67	2.68	25.38	6.18	5.72	20.79	3.23	63.08	.....	24.86	2.00			
	Mean	....	0.86	2.12	4.07	1.96	23.76	5.79	6.00	19.93	3.73	61.24	.....	24.28	1.54			
Yellow birch[3] (*Betula lutea*)...........	1	....	0.58	2.88	4.21	0.55	20.02	3.99	6.12	24.26	3.18	60.49	.....	28.40	1.11			
	2	....	0.57	2.58	3.87	0.67	20.20	4.39	6.03	25.40	3.12	61.08	.....	29.96	1.32			
	3	....	0.54	3.15	4.66	0.54	19.51	3.81	6.19	23.00	2.25	61.82	.....	26.55	1.04			
	4	....	0.37	2.06	3.15	0.63	19.65	5.02	5.92	25.86	2.21	61.85						
	Mean	....	0.52	2.67	3.97	0.60	19.85	4.30	6.07	24.63	2.69	61.31	.....	28.30	1.16			
Sugar maple[3] (*Acer saccharum*)........	1	....	0.46	2.60	4.27	0.29	16.98	4.26	7.22	21.10	2.50	60.78	.....	21.08	1.04			
	2	....	0.51	2.73	4.22	0.22	17.20	4.25	7.23	21.90	2.14	61.67	.....	25.82	1.05			
	3	....	0.40	2.94	4.78	0.30	18.04	4.60	7.25	22.21	2.05	60.20	.....	25.83	1.00			
	4	....	0.38	2.33	4.15	0.20	18.35	4.74	7.28	21.62	2.85	60.48	.....	25.20	0.77			
	Mean	....	0.44	2.65	4.36	0.25	17.64	4.46	7.25	21.71	2.39	60.78	.....	24.48	0.96			

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[1] G. J. RITTER and L. C. FLECK, *J. Ind. Eng. Chem.*, **14** (1922), 1050.

[2] S. A. MAHOOD and D. E. CABLE, *J. Ind. Eng. Chem.*, **14** (1922), 933.

[3] A. W. SCHORGER, *J. Ind. Eng. Chem.*, **9** (1917), 556.

Table 3.—Analyses of European Woods[1]

	Spruce (*Picea excelsa*), per cent	Pine (*Pinus silvestris*), per cent	Beech (*Fagus silvatica*), per cent	Birch (*Betula verrucosa*), per cent	Poplar (*Populus tremula*), per cent
Ash	0.77	0.39	1.17	0.39	0.32
Fat (*a*) Ether extract	0.78	1.92	0.31	0.71	1.08
Wax (*b*) Alcohol extract	1.52	1.53	1.47	1.09	2.08
(*c*) Sum of (*a*) and (*b*)	2.30	3.45	1.78	1.80	3.16
Resin (*d*) Alcohol-benzene extract	2.34	3.32	1.20	1.68	2.87
Methyl	2.36	2.20	2.96	2.77	2.57
Pectin (von Fellenberg)	1.22	1.11	1.75	1.61	1.82
Acetic acid (Schorger)	1.44	1.40	2.34	4.65	4.17
Protein (N × 6.25)	0.69	0.80	1.05	0.74	0.63
Furfural	7.49	7.04	14.90	16.08	12.64
Pentosan	11.30	11.02	24.86	27.07	23.75
Methylpentosan	3.00	2.23	1.02	0.84	0.72
Cellulose containing pentosan	63.95	60.54	67.09	64.16	62.89
Pentosan in cellulose	9.55	11.27	20.35	29.40	24.94
Cellulose corrected for pentosan	57.84	54.25	53.46	45.30	47.11
Lignin (hydrochloric acid method)	28.29	26.35	22.46	19.56	18.24

[1] C. G. Schwalbe and E. Becker *Z. angew. Chem.* **32** (1919). 229–231.

Table 4.—Analyses of European Woods[1]

(Results in per cent of dry weight)

Species	Protein (N × 6.25)	Resin and wax	Ash	Total pentosan	Hemicelluloses		Lignin	Cellulose[2]	
					Hexosans	Pentosans		Crude	Pure
1. Fir	1.21	2.83	1.10	11.48	13.58	8.67	29.17	43.44	40.62
2. Fir	1.21	1.71	0.42	11.63	13.00	9.74	27.98	45.95	44.06
3. Pine	1.27	3.17	0.53	10.80	12.78	8.70	29.52	44.01	41.93
4. Birch	1.29	2.47	0.68	25.86	4.61	23.20	23.27	44.52	41.85
5. Birch	2.29	1.88	0.46	24.01	5.00	21.48	26.38	42.50	39.97
6. Poplar	1.39	2.66	0.84	22.71	2.60	15.36	22.45	54.71	47.36
7. Poplar	1.14	2.32	1.21	21.88	3.43	15.10	20.75	56.06	49.27
8. Beech	1.58	0.70	0.96	24.30	4.36	17.79	22.69	51.93	45.41
9. Ash	1.30	2.24	0.83	23.68	5.70	19.29	26.01	44.64	40.24
10. Willow	1.17	2.04	0.83	23.31	5.05	16.75	24.70	49.46	42.91
11. Alder	1.89	2.83	0.49	22.94	3.65	15.90	24.57	50.69	43.64

[1] J. König and E. Becker, *Z. angew. Chem.*, **32** (1919), 155–160.

[2] Crude cellulose contains pentosans; pure is free from them.

in Table 5 than by the usual method of analysis. While being minor constituents, a summative analysis should include ash and protein. Information on the total pentosan content is lacking. There is also overlapping of mannan, for example, some of which remains in the Cross and Bevan cellulose. The extract with 5 per cent sodium hydroxide is meaningless as to composition. The extract is a mixture of a portion of the pentosans and other carbohydrates, acetic acid produced by hydrolysis of the acetyl groups of the lignin, protein, tannins, and other substances which give the lignin reaction. If a summation is desired it will be found by reference to Table 2 that addition of ash, hot-water-soluble, ether extract, acetic acid, pentosan, lignin, and cellulose (free from pentosan) gives a figure close to 100.

TABLE 5.—COMPOSITION OF WOOD

(Per cent of dry weight)

	Redwood	Western yellow pine	Sugar pine	Live oak
Benzene extract	0.34	2.22	2.84	0.52
Alcohol extract	4.39	1.49	1.90	4.52
Soluble in cold 5 per cent NaOH	......	......	......	19.53
Soluble in cold water	......	......	......	3.82
Cellulose	54.89	57.72	59.18	47.47
Lignin	34.50	29.47	29.50	21.14
Pentosans not otherwise accounted for	3.67	3.49	1.86	1.97
Mannan	3.21	6.37	6.63	0.00
Galactan	0.50	0.78	0.50	1.56
	101.50	101.54	102.41	100.53

According to Klason,[1] spruce (*Picea excelsa*) has the following composition:

	PER CENT
Cellulose (free from pentosans)	53
Hemicelluloses	15
Lignin	30
Fat, resin, protein, etc	2

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[1] P. KLASON, *Svensk Pappers-Tid.*, **24** (1921), 7.

Von Euler[1] gives the composition of pure coniferous wood substance as follows:

	Per Cent
Cellulose	54.10
Hemicelluloses:	
Hexosans	3.06
Pentosans	12.25
Lignin, including acetyl groups	30.60

The compostion of African wattle wood[2] (*Peltophorum africanum*) is not strikingly different from that of American hardwoods.

Effect of Storage on the Composition of Wood.—Time is of little influence on wood kept in a dry state. Schwalbe and Becker[3] were unable to detect any appreciable difference by chemical analysis between the wood (*Picea excelsa?*) of an Amati violin 260 to 280 years old and the wood used for violins in Germany at the present time.

Sawdust from Scotch pine stored for 2 years showed no appreciable change in ultimate composition. The wood had apparently undergone oxidation since the air from a pile of sawdust stored for 1 year contained 6.3 per cent by volume of carbon dioxide.[4] It should be remembered that the gas in the wood of a living tree is high in carbon dioxide.[5] Bergström[5] found 6.2 per cent of carbon dioxide and 15.4 per cent of oxygen in the gas taken from the sapwood of a growing Scotch pine and 5.0 per cent of carbon dioxide and 16.7 per cent of oxygen from that of a spruce.

Relation between Density of Wood and Its Cellulose Content. Griffin[6] concluded that there was no relation between the number of annual rings per inch and specific gravity, or between the specific gravity and yield of cellulose. It is a general rule, however, that the greater the number of rings per inch the greater will be the specific gravity. On a volume basis the wood with the greatest specific gravity will contain the most cellulose by weight. Wahlberg[1] found that the yield of pulp per solid cubic meter was 125 and 263 kilograms respectively for two spruce trees grown under apparently identical conditions, and 220 kilograms for a pine tree grown on poor soil. The percentage of cellulose based on the weight of dry, resin-free wood was very uniform.

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[1] A. C. von Euler, *Cellulosechemie*, **4** (1923), 1.

[2] E. F. English, *J. Soc. Chem. Ind.*, **43** (1924), 742B.

[3] C. G. Schwalbe and E. Becker, *Z. angew. Chem.*, **33** (1920), 272.

[4] H. Bergström, *Papier-Fabr.*, **22** (1924), 37.

[5] J. Böhm, *Landw. Vers.-Sta.*, **21** (1878), 372–388; H. Devaux, *Compt. rend.*, **134** (1902), 1366–1371.

[6] M. L. Griffin, *J. Ind. Eng. Chem.*, **6** (1914), 560–561.

The relation between the number of rings, specific gravity, and yield of cellulose has been investigated by Wahlberg.[2] The line of demarcation between the heartwood and sapwood of spruce is best developed by the use of a 1 per cent solution of osmic acid. The line did not extend equally in all radial directions, but the differences did not include more than one or two annual rings; on the other hand, it appeared from the twenty-third to the fifty-first ring in various trees. The following table shows clearly that the wood with the narrowest rings has the highest specific gravity. The apparent discrepancy between width of ring and specific gravity in Nos. 76 and 80 is probably due to the presence in the latter of a greater proportion of dense fall wood. A section of wood after drying *in vacuo* had a specific gravity of 0.345, while the average values for spring and fall wood were 0.307 and 0.601 respectively. From a comparison of

TABLE 6.—RELATION BETWEEN WIDTH OF RINGS AND DENSITY

No.	Annual rings	Average width of annual rings, millimeters	Specific gravity
72	59–54	1.6	0.434
73	53–49	1.8	0.408
74	48–44	3.4	0.395
75	43–40	2.9	0.357
76	40–38	6.2	0.307
77	38–35	4.8	0.333
78	34–31	4.2	0.345
79	30–27	5.1	0.341
80	26–23	6.8	0.353
81	23–10	4.1	0.341

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[1] H. E. WAHLBERG, *Papier-Fabr.*, **20** (1922), 1216–1218.

[2] H. E. WAHLBERG, *Zellstoff u. Papier*, **2** (1922), 129–134, 155–164, 202–212.

the density of certain rings and the weather for the paticular years which they represented, it is concluded that cold and wet weather leads to the formation of wood with a low specific gravity. This opinion cannot be generally accepted, as optimum growing conditions usually result in wide annual rings, hence a low specific gravity. No pronounced difference in ash content between spring and fall wood could be observed.

The cellulose in spring and fall wood was determined by a preliminary digestion with bisulphite solution, followed by treatment with bromine by Müller's method. It will be observed (Table 7) that after removal of the resin there is little difference between the cellulose contents of spring and fall wood in the trunk. The variations are within the experimental error of the methods employed.

TABLE 7.—CELLULOSE IN SPRING AND FALL WOOD

Annual rings	Cellulose in wood	
	Unextracted, per cent	Extracted with alcohol-benzene, per cent
Spring wood, 60–58	46.0	47.6
Spring wood, 47	47.8	49.0
Spring wood, 55–54	46.4	47.9
Fall wood, 55–52	48.0	49.5
Fall wood, 48–46	46.2	47.2
Fall wood, 34–33	46.7	48.1
Limb	39.4	42.1
Limb	40.3	42.9

Heartwood and Sapwood.—The effect of age on the chemical composition of alder wood (*Alnus glutinosa*) has been studied by Schwalbe and Becker[1] (Table 8). The differences between heartwood and sapwood are slight. The youngest wood contained the most protein, pectin, acetic acid, and pentosan, and the least cellulose and lignin.

Cieslar[2] determined the effect of various growth conditions on the lignin content of several conifers. He used the method of

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[1] C. G. SCHWALBE and E. BECKER, *Z. angew. Chem.*, **33** (1920), 14–16.

[2] A. CIESLAR, *Mitt. forstl. Versuchsw. Oesterr.*, **23** (1897), 1–40.

Benedict and Bamberger,[1] who assumed that oak contained 54.1 per cent[2] of lignin and 2.86 per cent methyl, CH_3, and that pure lignin contained 5.29 per cent methyl. These assumptions are incorrect, so that the conclusions of Cieslar must be interpreted as only indicating the degree of methylation and not lignification.

TABLE 8.—COMPOSITION OF ALDER WOOD (*Alnus glutinosa*)
(Per cent of dry weight)

	9 years	14 years		70 years	
		Middle rings	Outer rings	Heart-wood	Sap-wood
Ash	0.50	0.48	0.51	0.64	0.53
a. Ether extract	0.71	0.78	0.64	0.78	1.40
Alcohol extract (following *a*)	3.73	4.89	1.59	0.77	1.89
Methyl number	2.92	2.83	2.90	2.91	2.85
Methyl alcohol (von Fellenberg)	0.231	0.300	0.181	0.165	0.164
Pectin (von Fellenberg)	2.31	3.00	1.81	1.65	1.67
Acid hydrolysis (Schorger) Calculated as acetic acid	4.52	3.81	3.89	3.23	3.43
Actual acetic acid	4.20	3.59	3.63	2.89	3.24
Formic acid	0.24	0.17	0.20	0.17	0.15
Nitrogen	0.30	0.26	0.30	0.24	0.29
Protein (N × 6.25)	1.88	1.63	1.87	1.50	1.81
Furfural	14.76	14.06	14.04	13.55	11.04
Pentosan	25.15	23.98	23.95	23.10	18.85
Methylpentosan	0	0	0	0	0
Cellulose (Cross and Bevan)	56.22	58.00	61.58	58.35	59.75
Cellulose, pentosan-free	39.63	42.19	44.45	44.48	46.45
Lignin (Willstätter)	22.97	23.93	22.60	25.75	24.27

He concluded that the variation in lignin content within a species is greater than between different species. Spruce has more lignin within its natural range than in mild situations outside of it. Lignin decreases at the upper limit of tree growth. In spruce the lignin decreases from the base of the trunk to the top; the heartwood is richer in lignin than the sapwood and summer wood than spring wood. For equal volumes, rapidly grown wood contains less lignin than slowly grown wood. Abundant nourishment and favorable light conditions are conducive to lignin formation. Wood is richest in lignin where there is the greatest demand for mechanical strength.

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[1] R. BENEDICT and M. BAMBERGER, *Monatsh.*, **11** (1890), 260; *Chem. Ztg.*, **15** (1891), 221.

[2] E. SCHULZE, *Chem. Centr.*, **28** (1857), 321.

Von Euler,[1] using strong inorganic acids for isolating lignin, found that in the trunk of conifers the lignin varied from 25 to 33 per cent, and in branches even reached 36.5 per cent. Nine samples of wood, representing Scotch pine and Norway spruce, showed a lignin content varying from 26.80 to 31.35 per cent, the average being 28.63 per cent. The amount of lignin in a wood depends upon the age, part of the tree from which the sample is taken, and growth conditions. Klason[2] found the mean lignin content of a spruce 100 years old to be 26.6 per cent, while a tree 80 years old from the same forest contained 29.5 per cent. In the case of abnormal growths, such as "red wood," the lignin content may reach 37.1 per cent.

According to Johnsen,[3] cellulose decreases from the base to the top of the tree. A balsam fir 10.5 inches in diameter and having 64 annual rings showed an increase in cellulose from the pith to the sapwood.[4] The cellulose was determined by heating the wood in glycerine-acetic acid mixture, followed by chlorination. The sapwood of aspen contained 1.3 per cent more cellulose than the heartwood. The effect of abnormal growth is illustrated by the following analyses of balsam fir (Table 9). Rapid growth would appear to produce less cellulose than slow.

	Cellulose, Per Cent
A. Pith to fifteenth annual ring	51.14
B. From twentieth to thirty-fifth annual ring	53.26
C. Sapwood (outer 15 annual rings)	54.21

Table 9.—Effect of Abnormal Growth on Balsam Fir

	"Rotholz," per cent	Rapid growth, per cent	Slow growth, per cent
Cellulose	39.42	50.35	52.85
Alcohol extract	1.38	2.05	2.85
Lignin (with 72 per cent H_2SO_4)	33.60	24.44	24.85
Methyl, CH_3	2.74	2.43	2.62

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[1] A. C. von Euler, *Cellulosechemie*, **4** (1923), 2, 9.

[2] P. Klason, *Cellulosechemie*, **4** (1923), 81.

[3] B. Johnsen, *Pulp Paper Mag.*, **15** (1917), 333.

[4] B. Johnsen and R. W. Hovey, *J. Soc. Chem. Ind.*, **37** (1918), 132–137T.

TABLE 10.—ANALYSES OF SAPWOOD AND HEARTWOOD OF SOME AMERICAN WOODS[1]
(Results in percentage of oven-dry (105°C.) samples)

Species	Sample	Moisture	Ash	Solubility				Acetic acid	Methoxyl	Pentosan	Methylpentosan	Cellulose	Lignin	In cellulose				
				Cold water	Hot water	Ether	1 per cent NaOH							Pentosan	Methylpentosan	Alpha	Beta	Gamma
White ash:																		
No. 2 sapwood.......	179	5.34	0.61	5.81	6.41	1.17	21.77	3.23	4.70	19.85	2.40	50.38	26.95	18.83	1.60	74.67	13.67	11.66
No. 2 heartwood.....	180	5.45	0.30	2.24	3.40	0.43	19.59	2.31	5.36	19.90	2.25	53.56	27.39	16.75	1.34	64.68	24.58	10.84
No. 3 sapwood.......	181	4.91	0.57	5.25	7.02	0.88	21.93	3.70	5.66	20.16	2.63	49.72	27.39	19.67	1.60	55.11	28.29	16.50
No. 3 heartwood.....	182	7.42	0.32	2.12	4.46	0.46	18.97	2.66	5.20	19.87	2.46	53.40	28.38	17.34	1.47	42.45	33.22	24.33
Yellow poplar:																		
No. 1 sapwood.......	187	4.30	0.48	1.29	1.98	0.27	16.74	3.12	5.81	18.37	3.28	58.13	23.08	15.52	2.21	50.13	30.74	19.13
No. 1 heartwood.....	188	3.79	0.39	1.50	2.08	0.43	17.70	2.89	5.86	18.47	3.11	59.57	22.19	14.97	2.40	61.30	20.20	18.50
No. 2 sapwood.......	189	3.79	0.36	1.45	2.51	0.13	16.91	3.33	5.89	18.82	1.22	58.02	23.86	19.01	0.78	34.32	48.52	17.16
No. 2 heartwood.....	190	3.88	0.33	1.45	2.89	0.58	17.57	2.73	6.03	19.08	1.13	59.47	23.69	17.83	1.47	36.67	42.75	20.58
Pignut hickory:																		
No. 1 sapwood.......	191	3.54	0.40	4.91	6.45	0.29	19.11	3.58	5.56	18.18	1.11	56.08	21.87	16.90	1.30	51.55	21.92	26.53
No. 2 heartwood.....	192	3.90	0.45	2.07	2.95	0.36	15.10	3.08	5.79	18.64	1.02	58.81	22.85	16.20	1.39	59.44	23.74	16.82
Yellow birch:																		
No. 1 sapwood.......	207	4.92	0.26	1.05	1.98	0.48	16.77	2.34	5.66	21.36	1.66	58.91	24.69	20.72	1.13	52.15	32.90	14.45
No. 1 heartwood.....	208	4.76	0.40	4.16	5.69	0.81	20.51	1.78	5.46	20.37	1.39	56.88	24.62	21.87	1.12	61.17	23.23	15.60
No. 2 sapwood.......	213	4.28	0.18	1.74	2.10	0.88	19.78	3.75	5.47	22.30	1.82	56.57	27.76	22.19	1.71	52.40	26.82	20.78
No. 2 heartwood.....	214	4.36	0.23	2.76	3.96	0.99	21.14	2.83	5.27	23.21	1.07	54.93	28.13	21.81	1.04	53.56	25.00	21.44

White oak:																		
No. 1 sapwood.......	209	7.71	0.57	2.55	4.11	0.46	21.11	3.44	5.95	23.25	0.90	49.53	32.34	24.74	0.88	68.07	**15.27**	16.66
No. 1 heartwood.....	210	7.70	0.43	7.33	10.15	0.71	25.81	2.59	6.18	21.82	1.57	48.68	32.74	24.22	0.58	67.33	11.84	20.83
No. 2 sapwood.......	211	7.09	0.37	4.27	5.73	0.65	21.69	2.47	6.02	21.72	0.94	53.18	31.14	24.81	1.20	53.81	22.63	23.56
No. 2 heartwood.....	212	6.99	0.42	4.76	6.60	0.62	22.67	2.97	5.64	22.08	0.91	52.12	31.30	24.54	0.96	52.96	20.41	26.63
Bald cypress:																		
No. 1 sapwood.......	183	4.72	0.48	0.72	1.42	0.23	8.55	0.77	4.35	8.03	4.38	54.86	35.01	6.25	1.85	76.09	5.93	17.98
No. 1 heartwood.....	184	5.30	0.30	2.79	2.99	4.87	10.59	0.48	3.94	6.67	4.49	53.10	33.06	5.84	1.80	76.83	3.94	19.23
No. 2 sapwood.......	185	6.72	0.86	1.76	2.30	2.80	10.63	0.65	4.99	9.23	3.34	50.94	35.31	5.89	1.65	58.18	26.91	14.91
No. 2 heartwood.....	186	4.72	0.95	3.27	3.49	7.93	13.56	0.29	4.07	7.88	3.36	49.18	32.27	6.33	1.25	57.38	24.75	17.87
White pine:																		
No. 1 sapwood.......	193	3.90	0.23	3.55	5.15	5.46	17.16	1.68	4.16	9.31	2.14	54.25	26.51	6.81	2.09	54.56	17.47	27.97
No. 1 heartwood.....	194	2.92	0.42	5.97	7.68	3.62	19.15	1.43	4.60	8.56	1.00	50.23	26.14	7.12	2.02	57.29	22.42	19.29
Yellow cedar:																		
No. 1 sapwood.......	195	3.97	0.28	2.13	3.41	1.00	11.72	2.05	4.40	8.47	1.75	58.12	29.03	7.60	2.44	54.61	26.59	18.80
No. 1 heartwood.....	196	4.00	0.18	2.88	4.12	1.32	12.77	1.53	4.81	8.69	1.85	56.08	28.73	7.78	2.73	......	20.17	
White cedar:																		
No. 2 sapwood.......	197	5.59	0.64	2.18	2.82	.....	11.02	1.17	5.07	11.61	0.94	55.77	29.85	10.35	1.77	73.78	0.99	25.23
No. 2 heartwood.....	198	6.39	0.21	1.94	3.22	.....	11.41	0.84	5.00	10.79	1.72	55.19	31.39	8.52	1.58	61.47	22.23	16.30
No. 3 sapwood.......	199	6.02	0.48	3.02	3.96	1.44	12.71	1.11	5.23	10.82	1.16	55.02	32.14	8.95	1.28	69.17	14.04	16.79
No. 3 heartwood.....	200	6.48	0.27	2.80	4.01	1.87	14.14	0.74	5.09	10.36	1.56	54.42	32.42	7.97	1.32	55.22	24.74	20.04
Incense cedar:																		
No. 1 sapwood.......	205	6.46	0.47	1.92	2.97	0.67	11.16	1.33	5.95	12.08	0.45	49.09	34.73	10.14	1.24	50.69	12.98	36.33
No. 1 heartwood.....	206	7.27	0.30	4.74	7.08	4.78	19.99	0.68	6.21	12.04	0.56	44.53	33.67	11.68	1.31	66.62	11.05	22.33

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[1] G. J. Ritter and L. C. Fleck, *J. Ind. Eng. Chem.*, **15** (1923), 1055.

The most comprehensive investigation of the composition of heartwood and sapwood has been made by Ritter and Fleck[1] (Table 10). In the softwoods, the extracts with water, ether, and hot 1 per cent sodium hydroxide are higher in the heartwood than in the sapwood. Cellulose and lignin are correspondingly lower in the heartwood, though the lignin of white cedar forms an exception. The hardwoods may be divided into two groups, one having high extractives in the heartwood, and the other having high extractives in the sapwood. Where the extractives are high the cellulose is correspondingly low. In the hardwoods, with the exception of poplar, the lignin is higher in the heartwood than in the sapwood. Acetic acid by hydrolysis is in all cases higher in the sapwood than in the heartwood.

Much attention has been given to the transformation of sapwood into heartwood, but the reactions actually taking place are far from clear. The heartwood is usually sharply defined from the sapwood by its darker color, but in some species it is very difficult to distinguish a line of demarcation. The heartwood owes its darker color and higher specific gravity to the deposition of resins, gums, tannins, and related bodies that have undergone oxidation and other changes. In some cases, copious deposition of mineral substances takes place in the cells of the heartwood. Red beech under normal conditions does not form heartwood even in extreme old age. According to Hartig,[2] false heartwood is due to pathological effects, but it does not differ essentially from true heartwood.

The substance filling the cells of heartwood and giving it increased weight and color was called *xylochrome* by Hartig.[3] It was subsequently known as "Kernstoff." He thought that heartwood was formed by the transformation of the material originally present in the sap in the cells of the sapwood. Formation of heartwood in the *Amygdalœ* was assumed by various investigators[4] to be due to the deposition of cerasin which was formed by gummosis of the inner layers of the cell.

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[1] G. J. Ritter and L. C. Fleck, *J. Ind. Eng. Chem.*, **15** (1923), 1055.

[2] R. Hartig, "Das Holz der Rotbuche," Berlin (1888), p. 31.

[3] T. Hartig, cited by J. Gaunersdorfer, *Akad. Wiss. Wien*, **85**, I (1882), 9.

[4] A. Wigand, *Jahrb. wiss. Botanik*, **3** (1863), 115–179; H. Karsten, *Botan. Zeit.*, **15** (1857), 313–321; A. Trecul, *Compt. rend.*, **51** (1860) 621.

The observation that heartwood was more resistant to decay than sapwood led to the theory that it was formed as a protective measure, and that the darkening of living wood following an injury was the formation of "wound" or protective wood having the properties of heartwood.[1] Böhm[2] mentions that tyloses and deposits of gummy substances close the vessels and act as protective agents.

The changes occurring in the living wood of *Prunus avium* after wounding were followed by Temme.[3] The greenish-white color of the normal wood became yellow to reddish in 8 to 10 days. The color change was most intensive in the medullary rays. The latter contained numerous small brown grains attached to the cell well or surrounding the starch grains. In the brownest cells the starch had wholly or partially undergone transformation into the brown gum. Similar results were obtained with non-amygdalaceous trees, such as *Juglans regia*, *Quercus pedunculata*, and *Pyrus malus*. The gum was insoluble in water and potassium hydroxide and gave mucic and oxalic acids on oxidation with nitric acid. The gums, being colloidal, have a low diffusibility and remain at the point of origin. Wounding caused an increase in the specific gravity of the sapwood. The large amount of heartwood, which lowers the ability of the tree to transport water, may explain why the acacias are several weeks behind such trees as basswood and birch in their growth in spring.

Species	Specific gravity		
	Heartwood	Wound wood	Sapwood
Quercus pedunculata	1.604	1.130	0.946
Gleditsia triacanthos	1.574	0.657	0.202
Prunus avium	1.677	2.187	1.512
Pyrus malus	1.648	1.523	1.162
Juglans regia	1.177	1.155	1.100

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[1] B. Frank, *Ber. botan. Ges.*, **2** (1884), 330; *cf.* C. Kraus, *Ibid.*, p. LIII.

[2] J. Böhm, *Botan. Zeit.*, **37** (1879), 229.

[3] F. Temme, *Landw. Jahrb.*, **14** (1885), 465–484.

Herrmann[1] and Tuzson[2] agree with Hartig that the formation of false heartwood is pathological. Irritation of the sapwood leads to the formation of tyloses and gums, which retard the penetrance of mycelia. Von Tubeuf[3] was of the opinion that wound wood had no protective action against fungi, and Will[4] denied that there is necessarily an analogy between heartwood and wound wood. In the latter, the protective agency is a substance resembling bassorin which does not occur in heartwood.

Heartwood is not necessarily protective. The "brown" heartwood of English oak (*Querus robur*) as distinguished from normal heartwood is due to a fungus which appears to subsist mainly on tannin.[5]

According to Gaunersdorfer,[6] the first step in the formation of heartwood consists in filling the wood elements with various solid substances, principally starch. The parenchymatous tissues are rich in tannic acid, which appears to be an intermediate body between starch and the final deposits that form the heartwood. Formation of heartwood is due to various tannins, gums, and resins which differ with the species of wood.

The problem of heartwood formation has been studied more recently by Münch.[7] The brown deposits are not due to secretions from the wall of the living cells, but to oxidation of the cell contents after death ensues. The same deposits are formed in cells after being attacked by fungi, so that they cannot serve as a protection against them. A certain amount of moisture in addition to oxygen is necessary to produce the brown color. Heartwood and protective wood are formed from the same cause. Oxygen cannot penetrate the plasma membrane, so that the contents of living cells are not colored. The fact that heartwood, normal and pathological, is specifically heavier and richer in heartwood substance is due to the occurrence of an extraordinary influx of food materials into the living cells surrounding dead portions of wood, so that the activity of the cambium is increased sevenfold. Just how this reasoning applies to heartwood is not clear. All cells in wood except those in the thin cambium layer, wood parenchyma, and medullary rays are dead. The only means of transporting food materials to the interior of the tree is through the medullary rays which are always surrounded by dead cells.

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[1] E. Herrmann, *Z. Forst-u. Jagdwesen,* **34** (1902), 596–617.

[2] J. Tuzson, "Anatomische und mykologische Untersuchungen über die Zersetzung und Konservierung des Rotbuchenholzes," Berlin (1905), 89 pp.

[3] K. F. von Tubeuf, *Z. Forst-u. Jagdwesen,* **21** (1889), 385.

[4] A. Will, "Beiträge zur Kenntnis von Kern-und Wundholz," Diss. Bern (1899), 92 pp.

[5] P. Groom, *Ann. Botany,* **29** (1915), 393–408.

[6] J. Gaunersdorfer, *Akad. Wiss. Wien,* **85,** I (1882), 9–41.

[7] E. Münch, *Naturwiss. Z. Forst-u. Landw.,* **8** (1910), 533–547; 553–569.

The formation of heartwood in "sugi" (*Cryptomeria japonica*) is attributed to the darkening of a substance resembling catechol.[1] Catechol or a related compound appears to be widely distributed in plants. Alkalis promoted coloration while acids and rapid seasoning prevented it. In the presence of air and moisture ammonia is evolved by decomposition of the protein in the wood, thus producing favorable conditions for oxidation of the phenols. Tinkler[2] suggests that the reddish-brown color of oak may be due to a reaction between a nitrogenous compound and tannin, and partly to the presence of phlobaphene. If the rapidity with which an alkaline solution of pyrogallol absorbs oxygen and turns dark is recalled, this forms an acceptable explanation for the darkening of wood. Furthermore, it has been observed that the catechin content of the wood of *Acacia catechu* decreases during storage and in the standing tree at certain stages.[3]

The conspicuous black deposit in the heartwood of ebony (*Diospyros ebenum*) has been examined by numerous investigators. Molisch[4] supposed that the inner layers of the cell wall changed into a gum which subsequently underwent humification. The heartwood contained 4.63 per cent of humic acid and 1.30 per cent of carbon (Humuskohle). The contention that the "carbon" was formed by reduction[5] and that it actually was carbon was disputed by Praël,[6] since it could be rendered colorless by a mixture of potassium chlorate and hydrochloric acid. Will[7] supports this view since nitric acid also rendered it colorless. Hanausek[1] has found a black substance, phytomelane, in the pericarp of a large number of compositæ. The substance resembles the black deposit in ebony. Its resistance to oxidizing agents, even chromic acid, indicates a high carbon content.

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[1] M. Fujioka and K. Takahashi, *J. Forestry*, **19** (1921), 844–866.

[2] C. K. Tinkler, *Biochem. J.*, **15** (1921), 477.

[3] P. Singh, *Ind. Forester*, **41** (1915), 482–485.

[4] H. Molisch, *Akad. Wiss. Wien*, **80,** I (1879), 54–83.

[5] A. Belohoubek, *Botan. Centr.*, **18** (1884), 293.

[6] E. Praël, "Vergleichende Untersuchungen uber Schutz-und Kernholz," Diss. Rostock (1888).

[7] A. Will, Diss. Bern (1899), p. 81.

Ash.—The composition of the ash of representative woods will be found in Tables 11 and 12. The ash content of domestic woods generally falls within the limits 0.2 to 1.0 per cent. Some exotic woods contain 4 to 5 per cent. There is no relation between ash content and specific gravity. Balsa, one of the lightest of woods, contains 2.0 per cent of ash.

The ash in wood appears to be either strongly adsorbed or combined with organic and inorganic matter in an insoluble form. A portion can be extracted with water. Finely powdered logwood contained 2.32 per cent of ash in the original state and 2.03 per cent after leaching.[2] Schroeder[3] reduced the ash content of spruce from 0.232 to 0.183 per cent by leaching with water. Sacc[4] digested fir wood with hydrochloric acid and succeeded in reducing the ash from 0.55 to 0.07 per cent. Wood boiled for a long time with sulphuric acid gave an ash that still contained salts of the alkalis.[5] Berthelot[6] found that wood charcoal heated with 1 per cent hydrochloric acid at 100° retained 5 to 6 per cent of its total potassium and 5 per cent of its calcium which are present as organic compounds. Insoluble potassium salts are present in the leaves of oak but only in traces, if at all, in the trunk.[7]

Crystalline deposits, especially calcium oxalate, are of frequent occurrence in heartwood. Crystals of calcium oxalate occur in *Juglans, Hicoria, Diospyros,* and all species of *Quercus.* They are particularly abundant in the live oaks.[8] The vessels of

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[1] T. F. Hanausek, *Akad. Wiss. Wien,* **116,** I (1907), 3–31; *Ber. botan. Ges.,* **29** (1911), 558–562.

[2] F. H. Storer, *Bull. Bussey Inst.,* **2** (1877–1900), 44.

[3] J. Schroeder, *Thar. forstl. Jahrb.,* **24** (1874), 55.

[4] F. Sacc, *Ann. chim. phys.,* [3] **25** (1849), 223.

[5] C. Bischof, *J. prakt. Chem.,* **47** (1849), 196.

[6] M. Berthelot, *Compt. rend.,* **141** (1905), 798.

[7] M. Berthelot, *Compt. rend.,* **142** (1906), 313.

[8] S. J. Record, "Economic Woods of the United States," N. Y. (1912), p. 21.

Sideroxylon cinereum, a tropical tree noted for its hardness, contains large crystals of calcium oxalate.[1]

TABLE 11.—COMPOSITION OF ASH OF GEORGIA WOODS[1]

	Ash[2]	K_2O	Na_2O	CaO	MgO	P_2O_5	SO_3	Cl	SiO_2	Fe_2O_3	C	CO_2
Carya tomentosa........	0.73	18.93	3.38	25.21	6.66	7.98	2.06	0.28	1.80	0.25	1.20	32.44
Quercus rubra..........	0.85	16.41	3.68	32.25	3.58	7.04	2.29	0.68	0.97	0.21	1.38	31.85
Quercus alba............	0.37	29.90	1.94	21.21	2.43	6.72	4.11	1.00	3.20	0.50	3.87	25.16
Quercus obtusiloba......	1.09	15.46	7.22	32.67	4.84	6.38	0.38	0.77	1.00	0.37	0.65	28.86
Pinus mitis.............	0.35	12.97	1.18	43.31	2.11	2.75	0.86	0.67	2.35	0.18	0.74	33.26
Cornus florida..........	0.95	20.03	7.65	27.81	4.92	1.02	2.72	0.74	2.00	0.12	0.40	28.16
Fraxinus americana....	0.43	34.74	0.94	17.68	0.45	2.69	8.58	0.26	7.05	2.92	1.14	23.65
Castanea vulgaris.......	0.22	13.33	7.67	36.43	1.56	5.00	2.68	0.88	4.17	2.65	1.19	24.82
Platanus occidentalis....	0.99	18.24	5.92	24.98	0.49	9.65	5.73	0.45	9.66	4.13	2.14	19.01
Pinus palustris.........	0.49	10.34	2.34	37.24	4.21	2.65	4.32	0.21	3.41	2.76	1.11	31.47
Magnolia grandiflora...	0.60	11.87	2.52	23.64	4.89	5.31	3.46	0.23	7.32	1.60	17.22	22.16

[1] H. C. WHITE, *Ga. Agr. Exp. Bull.*, **2** (1889), 17–26; **3,** 50–53.

[2] Based on wood with 10 per cent moisture.

TABLE 12.—COMPOSITION OF ASH OF HEARTWOOD AND SAPWOOD[1]
(Results based on 10,000 parts of dry wood)

	Ash[2]	K_2O	P_2O_5	CaO	MgO	Fe_2O_3	SO_3	SiO_2	Na_2O
Larch:									
Sapwood...............	0.22	5.32	1.28	6.84	3.33	1.10	1.27	1.08	0.90
Heartwood.............	0.12	2.97	0.15	4.03	1.94	0.93	0.55	0.25	0.59
Pine:									
Sapwood...............	0.19	5.40	1.37	5.25	2.09	1.19	0.98	0.39	0.87
Heartwood.............	0.15	2.30	0.13	6.28	2.41	0.83	0.68	0.52	0.47
Spruce:									
Sapwood...............	0.26	9.80	2.87	5.54	1.46	1.54	1.11	0.92	0.38
Heartwood.............	0.20	5.93	0.20	7.36	1.96	1.71	0.86	0.20	0.65
Oak:									
Sapwood...............	0.42	19.56	5.22	6.93	2.63	1.46	2.90	0.56	1.13
Heartwood.............	0.16	6.71	0.43	4.08	0.44	0.51	1.98	0.88	0.24
Beech:									
Sapwood...............	0.47	19.24	2.15	12.56	6.77	1.65	1.93	0.59	0.53
Heartwood.............	0.40	15.47	0.60	13.33	5.11	0.82	1.55	0.82	0.17

[1] W. DAUBE, *Forstliche Blätter*, **20** (1883), 177.

[2] Per cent of dry wood.

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[1] H. MOLISCH, *Akad. Wiss. Wien*, **80,** I (1879), 75.

Baker[1] examined 22 orders of Australian trees and found crystals of calcium oxalate in 15 of them. Usually only one crystal occurs in a cell. The "grit" of *Eucalyptus pilularis* and *Tristania conferta* is due to silica. Molisch[2] found copious deposits of calcium carbonate in the heartwood of *Ulmus, Celtis, Fagus,* and other genera. The pith of *Populus alba* contained 38.9 per cent ash. The principal deposition of crystalline calcium carbonate takes place in the heartwood, owing to its lower conductivity; as the solution of calcium bicarbonate slowly rises carbon dioxide escapes, due to the increased temperature, calcium carbonate being deposited. The heartwood of red carrabeen (*Geissois benthami*) contains deposits of calcium carbonate which in some cases form 18 per cent of the weight of the wood.[3] Cracks in the wood of *Hieronyma alchorneoides* from Trinidad contained a deposit, of which 85.8 per cent was calcium carbonate.[4]

In general, the sapwood contains more ash than the heartwood, which is to be expected, since it contains the tissues engaged in the transportation of water and foodstuffs. Daube[5] (Table 12) found the most ash in the sapwood where potassium, phosphorus, and sulphur were most abundant. Excessive deposition of calcium in the heartwood may reverse the ash content. Zimmermann[6] found the distribution of ash in a beech (*Fagus silvatica*) 94 years old to be as follows:

Annual rings	1–15	15–25	25–35	35–45	45–60	60–83	83–94 (sapwood)
Ash, per cent	1.162	0.827	0.645	0.612	0.555	0.458	0.205
$CaCO_3$	0.579	0.251	Trace	Trace			

The ash is most abundant in the roots where the transportation of water begins and in the twigs where it ends. In the trunk the ash decreases from the base upwards. In general, there is little variation in a given portion of the wood throughout the year.[1]

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[1] R. T. Baker, *J. Proc. Roy. Soc. N. S. Wales*, **51** (1917), 435–444.

[2] H. Molisch, *Akad. Wiss. Wien.*, **84**, I (1881), 7–28.

[3] T. Steel, *Proc. Linnean Soc. N. S. Wales*, **46** (1921), 489.

[4] J. H. Hart, *Ann. Botany*, **1** (1887), 361–362.

[5] W. Daube, *l.c.*

[6] H. Zimmermann, *Z. angew. Chem.*, **6** (1893), 426–428.

The rôle of the inorganic constituents is not definitely known. In spite of the composition of the soil the constituents are usually taken up selectively. The ash of pines growing in a sandy soil is low in silica and high in lime (Table 11). The potash content varies from 10 to 35 per cent. In general, the hardwoods are highest in potash but there are numerous exceptions. According to Sieber,[2] during the formation of buds, calcium decreases in the cambium and potassium increases. During the period of assimilation, the calcium increases and by summer may double in amount. Lime may form 75 per cent of the total ash. The following values are given by Wolff:[3]

	CaO		CaO
Tilia grandifolia	75.92	*Ulmus campestris*	77.31
Robinia pseudacacia	58.30	*Fagus silvatica*	60.25
Fraxinus excelsior	62.14	*Quercus pedunculata*	76.27
Populus tremula	66.50	*Sorbus aucuparia*	76.13
Abies pectinata	10.17	*Picea excelsa*	29.41

Ebony (*Diospyros ebenus*) contains 3.92 per cent ash, of which 90 per cent is calcium carbonate.[4]

Magnesium, manganese, iron, aluminum, chlorine, sulphur, phosphorus, and silicon usually form only a minor portion of the ash. Manganese appears to be an essential constituent and in some cases occurs in large amounts. Schroeder[5] found 22.47 per cent Mn_3O_4 in the ash of *Picea excelsa* and as much as 40 per cent in that of *Abies pectinata*. Guerin[6] extracted from various woods a nitrogenous product high in manganese. According to Teicher,[7] plants growing in wet situations contain more manganese than those growing on higher ground; conifers contain more manganese than the hardwoods. The ash of teak wood (*Tectona granda*) consists largely of calcium phosphate.[1] Frankforter[2] reports the presence of metallic copper in an oak tree at Minneapolis. In the last six to seven annual rings the copper could be seen with the naked eye.

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[1] The ash content of trees has been extensively investigated from all angles. Consult: E. Wolff, "Aschen-Analysen," Berlin, Part I (1871), 194 pp. and Part II (1880), 170 pp.; F. Czapek, "Biochemie der Pflanzen," Jena, 2 (1920), 400–414.

[2] F. W. Sieber, *Verhandl. phys.-med. Ges. Würzburg*, **41** (1912), 11.

[3] E. Wolff, *l.c.*

[4] H. Molisch, *Akad. Wiss. Wien*, **80**, I (1879), 70.

[5] J. Schroeder, *Thar. forstl. Jahrb.*, **24** (1874), 275.

[6] G. Guerin, *Compt. rend.*, **125** (1897), 311.

[7] Teicher, *Cellulosechemie*, **2** (1921), 64.

Aluminum is usually present in very small amounts. The "silky oak" (*Orites excelsa*) is exceptional; its ash (0.7 per cent) contains 40 to 80 per cent of alumina.[3] The metal occurs in the wood as basic aluminum succinate. A trace of cobalt was found in the ash from one specimen.

Pectin.—The nomenclature of pectin and its related compounds is confusing and greatly in need of standardization. According to von Fellenberg,[4] there are three compounds, pectose pectin, and pectic acid, that must be considered. Pectose or protopectin occurs in unripe fruits. It is converted into soluble pectin by ripening, and by boiling with water or dilute acids. Alkalis convert it into a salt of pectic acid, from which pectic acid is obtained on acidifying. Schryver and Haynes[5] claim that there is but a single acidic substance, pectinogen, to be obtained from all sources. Weak alkalis convert it to pectin from which gels can be obtained. Addition of lime water or calcium chloride precipitates the pectin quantitatively. The actual existence of protopectin is doubted by Tutin,[6] since he found that if the cell structure of green apples was sufficiently destroyed all the pectin could be removed with cold water. Sucharipa,[7] on the other hand, furnishes evidence that in the rind of *Citrus* the protopectin is combined with cellulose.

It is highly probable that various pectins occur in nature. Von Fellenberg[8] was the first to observe that pectin gives methyl alcohol on treatment with dilute alkali. He considered pectin to be the methyl ester of pectic acid. While fruit pectins give about 10 per cent of methyl alcohol, that from pea pods contains only 1.9 per cent.[1] In flax, the methoxyl content of the pectin varies with the part of the plant from which the pectin is obtained and the treatment which it has received.[2]

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[1] G. Thoms, *Landw. Vers.-Stat.*, **23** (1879), 413.

[2] G. B. Frankforter, *Chem. News*, **79** (1899), 44.

[3] H. G. Smith, *J. Proc. Roy. Soc. N. S. Wales*, **37** (1903), 107–120.

[4] T. von Fellenberg, *Mitt. Lebensm. Hyg.*, **5** (1914), 225.

[5] S. B. Schryver and D. Haynes, *Biochem. J.*, **10** (1916), 539–547.

[6] F. Tutin, *Biochem. J.*, **17** (1923), 510–514.

[7] R. Sucharipa, *J. Am. Chem. Soc.*, **46** (1924), 145–156.

[8] T. von Fellenberg, *Mitt. Lebensm. Hyg.*, **4** (1913), 122, 273.

Tutin[3] found that acetone, also, was obtained by treating pectin with $0.1N$ sodium hydroxide at room temperature. The ratio of acetone to methyl alcohol was 1:2. Both compounds are believed to be present as ester groupings, the acetone in its enolic form,—$CH_3.C(OH):CH_2$. Pectin is probably the dimethyl-isopropenyl ester of pectic acid.

It has long been known that pectin contains araban and gives mucic acid on oxidation. The most illuminating work on the constitution of pectin is the paper of Ehrlich.[4] Crude pectin from beets consists of the calcium and magnesium salts of pectic acid. Pure pectic acid contains about 9 per cent of methyoxyl and is practically free from pentoses, though it gives furfural on distillation with acids, and shows the pentose reaction with orcinol and resorcinol. Limited hydrolysis with dilute oxalic acid gives *d*-galactose-galacturonic acid, $C_{12}H_{20}O_{12}$. Sodium hydroxide produces *d*-tetragalacturonic acid, $C_{24}H_{34}O_{25}$, which shows the color reactions for pentoses and glucuronic acid. Pectin in nature is the calcium-magnesium salt of an anhydro-arabino-galactose-methoxyltetragalacturonic acid.

Nanji[5] recognizes only pectinogen and pectic acid which is formed by de-esterification. The basal molecule consists of one anhydroarabinose group, one anhydrogalactose group, and four galacturonic acid groups. Methylpentoses are absent. Iron is a more important constituent of the pectinogen than calcium or magnesium.

Only small amounts of pectin exist in wood. Von Fellenberg[6] obtained about 0.05 per cent of methyl alcohol (0.5 per cent pectin) by the alkaline hydrolysis of fir wood. Pectic acid could not be detected nor could pectin be obtained by heating the wood with water or 1 per cent tartaric acid at 120°. The derivative yielding methyl alcohol is, accordingly, not identical with fruit pectin. There is more pectin in young wood than in old and more in hardwoods than in conifers. The wood of an ash seedling contained 1.6 per cent pectin. Schwalbe and Becker,[1] using von Fellenberg's method, found 3.0 per cent of pectin in alder wood. Nanji[2] determines pectin by taking advantage of the property of uronic acids of forming carbon dioxide when distilled with 12 per cent hydrochloric acid. By this method the cereal straws were found to contain 6.8 to 9.5 per cent of pectin. In wood and straw, only a portion of the pectin is soluble in oxalic acid solution. O'Dwyer[3] has recently isolated from beech wood a small amount of a pectic substance.

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[1] R. G. W. Farnell, *Int. Sugar J.*, **25** (1923), 248–251.

[2] E. Correns, *Faserforschung*, **1** (1921), 229–240.

[3] F. Tutin, *Biochem. J.*, **15** (1921), 494–497.

[4] F. Ehrlich, *Chem. Ztg.*, **41** (1917), 197–200.

[5] D. R. Nanji, F. J. Paton, and A. R. Ling, *J. Soc. Chem. Ind.*, **44** (1925), 253–258T.

[6] T. von Fellenberg, *Biochem. Z.*, **85** (1918), 82; *Mitt. Lebensm. Hyg.*, **8** (1917), 1–29.

Our chief interest in pectin lies in its relation to lignin and the middle lamella which botanists believe consists of modified pectin. Treub[4] suggested that in cell division the protoplasmic cell plate splits to form the plasma membrane of the two daughter cells. Between these membranes is secreted a substance which becomes the primary layer or middle lamella. This view has been confirmed by Timberlake[5] and Allen.[6]

The generally accepted view as to the chemical composition of the newly formed cell walls are due principally to Mangin.[7] He found that the middle lamella consisted of pectose, on which was deposited a secondary layer of cellulose. The various layers rarely exist in a pure form and soon undergo profound modification. The pectose of the primary layer changes to insoluble calcium pectate, while that in the secondary and tertiary layers is transformed into lignin; reactions for cellulose are then no longer obtained.

It was found by von Fellenberg[8] that the youngest growth of ash was rich in pectin but poor in lignin. His passing suggestion that the young growth changes to wood poor in pectin and rich in lignin is worthy of careful consideration; both pectin and lignin are high in carbon and methyl groups and both are associated with pentosans and galactan.

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[1] C. G. Schwalbe and E. Becker, *Z. angew. Chem.*, **33** (1920), 14.

[2] D. R. Nanji *et al.*, *l. c.*

[3] M. H. O'Dwyer, *Biochem. J.*, **19** (1925), 694–696.

[4] M. Treub, "Quelques recherches sur la rôle du noyau dans la division des cellules végétales," Amsterdam (1878).

[5] H. G. Timberlake, *Botan. Gaz.*, **30** (1900), 73–99; 154–170.

[6] C. E. Allen, *Botan. Gaz.*, **32** (1901), 1–34.

[7] L. Mangin, *Compt. rend.*, **107** (1888), 144–146.

[8] T. von Fellenberg, *Biochem. Z.*, **85** (1918), 88, 94.

Both pectose and pectic acid are associated with the cellulose.[1] When sections were treated with acid-alcohol mixture, then stained with a pectic acid stain such as methylene blue, Bismark brown, or other basic dye, the middle lamella stained strongly while the pectin in the cellulose layers was much less strongly colored. Mangin inferred that a neutral pectin occurred with the cellulose and that there was a salt of pectic acid in the middle lamella. Thin sections were treated with acid-alcohol mixture, washed with water, and immersed in an alkaline solution.[2] After a short time the mass was agitated and filtered. Acidification of the filtrate produced a gelatinous mass of pectic acid.

According to Devaux,[3] the middle lamella does not consist of calcium pectate but of pectose. The latter is hydrolyzed by an alcoholic solution of hydrochloric acid and also by heating with water for a few minutes. The soluble pectin thus produced is transformed into pectic acid by alkalis. The cell wall contains several pectoses, which under the action of reagents show different resistances to transformation into pectin.

Devaux[4] observed that pectic compounds reacted with salts of the heavy metals to give a salt of pectic acid, while lignified tissues were scarcely affected until after treatment with hypochlorite solutions. A section is plunged into a solution of a ferric salt, then washed with water and finally with a 2 per cent solution of acetic acid. The iron is invisible, but is brought out by immersion in a solution of potassium ferrocyanide. The blue color produced is accentuated by a drop of hydrochloric or nitric acid. The coloration is especially strong for the soft tissues. After washing with dilute acid, the lignified tissues are so feebly colored that the wood can be stained with safranin, thus producing double colorations.

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[1] L. Mangin, *Compt. rend.*, **109** (1889), 579–582.

[2] L. Mangin, *Compt. rend.*, **110** (1890), 295–297.

[3] H. Devaux, *Mem. soc. sci. phys. nat. Bordeaux*, [6] **III** (1903), 89.

[4] H. Devaux, *Act. Soc. Linn. Bordeaux*, [VI] **6** (1901), XXXIII, LVIII, and LXXXII.

Mangin[1] found in ruthenium red, $Ru_2(OH)_2Cl_4.7NH_3.3H_2O$, what he considered to be a specific stain for pectin. Lignin is not colored strongly until after treatment with alkalis or hypochlorites. In addition to pectin, ruthenium red stains gums, mucilages, nitrogenous compounds, and the cuticle of cotton, but not the cutinized membranes of leaves and twigs. The color with pectins is unaffected by glycerine and alcohol. An aqueous solution of the stain of a concentration of 0.005 per cent is satisfactory.

Stains seldom furnish satisfactory information as to chemical composition. It may well be doubted if ruthenium red is specific and capable of distinguishing between lignin and pectin. Phloroglucinol-hydrochloric acid, which is a reagent for lignin, stains the middle lamella of lignified elements, *e.g.*, *Tilia*, *Quercus*, and *Pinus*, more deeply than the secondary membranes.[2] Whatever may be the relation between pectin, lignin, and the middle lamella from a botanical standpoint, there is at present no striking chemical analogy apparent between lignin and pectin. The galacturonic acid groups of the pectin are so profoundly modified in lignin that they are no longer capable of giving mucic acid on oxidation. The methyl groups having an ester linkage in pectin have an ether linkage in lignin. These changes take place with such rapidity in the cambium, which at best forms only a small portion of the wood, that it is impossible to follow them by ordinary chemical methods. The solution will probably have to await further development in the technique of microchemical analysis.

Sachsse[3] looked upon lignin as a transformation product of cellulose. This hypothesis has been supported by others.[4] According to König and Rump,[5] lignin is formed by the addition of alkyl groups to cellulose. The changes must be more profound, since trimethylcellulose contains only 53 per cent of carbon while they report 68.75 per cent for wood lignin.

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[1] L. Mangin, *Compt. rend.*, **116** (1893), 653–656.

[2] F. C. von Faber, *Ber. botan. Ges.*, **22** (1904), 180.

[3] R. Sachsse, "Die Chemie und Physiologie der Farbstoffe, . . . " Leipzig (1877), p. 133.

[4] C. F. Cross and E. J. Bevan, "Cellulose" (1895), p. 179; A. G. Green, *Z. Farben-u. Textilchem.*, **3** (1904), 97; K. Fromherz, *Z. physiol. Chem.*, **50** (1907), 210.

[5] J. König and E. Rump, "Chemie . . . Pflanzen-Zellmembran" (1914), p. 83.

There is also the hypothesis that lignin is derived from pentoses.[1] Klason[2] believes that lignin, like the tannins to which it is closely related, may exist in wood as a glucoside. The parent substance, dihydroxycinnamyl alcohol, may be formed from the pentoses as follows:

$$\underset{\text{Pentose}}{2C_5H_{10}O_5} = \underset{\text{Dihydroxycinnamyl alcohol}}{C_9H_{10}O_3} + 5H_2O + CO_2.$$

Methylation of the phenolic groups may take place through formaldehyde:

$$R.OH + CH_2O = R.OCH_3 + O.$$

The oxygen liberated changes R.H into R.OH and oxidizes allyl alcohol complexes into the corresponding aldehyde and acid complexes occurring in lignin. A similar derivation is assumed by von Euler.[3] Coniferyl alcohol, formed from pentoses, is the source of related alcohols and aldehydes, which condense to form α-lignin, and related acids which form β-lignin and tannic acids.

Strupp[4] has recently elaborated a derivation of lignin from the cyclic sugars, such as pinite and inosite.

Starch.—Starch in small amounts appears to be found locally throughout the entire trunk of the tree. According to Sinnett,[5] it is most abundant in winter in the thick-walled, well-lignified cells remote from the centers of formation.

During the dormant period starch is stored in the living cells of the pith, wood parenchyma, and medullary rays.[6] When vegetation begins it appears in the bark tissues. With the formation of leaves the starch disappears from the bark, wood parenchyma, medullary rays, and pith in the order given. A portion may never be used during the growth of the tree, but is occluded in cells changed into heartwood, where it may remain indefinitely. This starch is considered as rendering the wood susceptible to decay. It has never been shown that starch influences durability; it is a popular belief, however, that wood felled in summer is best, since it contains the least starch at this season. Experiments conducted in Germany showed that the month of felling was without influence on durability.[1] Western larch is a comparatively durable wood, although it contains a large amount of an analogous carbohydrate, galactan.

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[1] K. G. Jonas, *Z. angew. Chem.*, **34** (1921), 290; B. Rassow and A. Zschenderlein, *Ibid.*, p. 204.

[2] P. Klason, *Arkiv Kemi, Mineral. Geol.*, **6**, No. 15 (1917), 20; *cf. Ber.*, **55** (1922), 454.

[3] A. C. von Euler, *Cellulosechemie*, **3** (1922), 3; *cf.* C. A., **15** (1921), 2470.

[4] E. Strupp, *Cellulosechemie*, **5** (1924), 6.

[5] E. W. Sinnett, *Botan. Gaz.*, **66** (1918), 162.

[6] W. A. Price, *Ohio J. Sci.*, **16** (1916), 356.

Hartig[2] believed that the greater part of the starch stored in autumn was held against the fruiting season, during which it disappeared rapidly and completely. Spring growth exhausted only the starch in the one or two youngest annual rings.

The data available on the starch content of woods are meager, and generally misleading, owing to faulty methods of analysis. Methods based on acid hydrolysis[3] are in some cases grossly incorrect, as pentosans and other hemicelluloses are hydrolyzed simultaneously with the starch. Du Sablon[4] used acid hydrolysis for determining the variation in starch content of various fruit and forest trees throughout the year. The trunk wood of chestnut, *e.g.*, is credited with 17.6 to 24.2 per cent of starch.

The suggested correction for pentoses[5] does not provide for hexosan hemicelluloses.

The use of diastase[6] or takadiastase[7] likewise does not give accurate results.[8]

The best data available indicate that the starch content of wood does not exceed 3 to 4 per cent. In mature forest wood it is probably considerably lower. The wood of the pear tree contained 3.07 per cent of starch.[1] Tottingham and Gerhardt[2] found that digestion with saliva was the most reliable method. Young branches of apple and plum trees contained 3.3 and 3.9 per cent of starch respectively. Beckmann[3] determined the amount of starch in trees felled in autumn and found:

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[1] WAGNER'S *Jahresber.*, **29** (1883), 1200.

[2] R. HARTIG, *Botan. Zeit.*, **46** (1888), 837–842.

[3] "Methods of Analysis A. O. A. C." Washington (1920), p. 95; VON WISSEL, *Landw. Jahrb.*, **53** (1919), 617; *cf.* A. MANARESI and M. TONEGUTTI, *Staz. sper. agrar. ital.*, **43** (1910), 705.

[4] L. DU SABLON, *Compt. rend.*, **135** (1902), 866; **140** (1905), 1608; *Rev. gen. botan.*, **16** (1904), 341; **18** (1906), 5, 82.

[5] S. WEISER and A. ZAITSCHEK, *Arch. Physiol.*, **93** (1903), 98.

[6] H. W. WILEY and W. H. KRUG, *J. Am. Chem. Soc.*, **20** (1898), 253, 266.

[7] W. A. DAVIS and A. J. DAISH, *J. Agr. Sci.*, **6** (1914), 152.

[8] F. E. DENNY, *J. Assoc. Official Agr. Chem.*, **6** (1922), 175; W. E. TOTTINGHAM and F. GERHARDT, *J. Ind. Eng. Chem.*, **16** (1924), 139.

Species	Starch, Per Cent
Maple	2.65
Birch	0.95
Alder	1.54
Elm	5.90
Sweet chestnut	2.65

The starch was determined by exhausting the finely powdered wood with water at 108 to 110° for 8 hours and subsequently heating the filtrate (100 cubic centimeters) with 10 cubic centimeters of 25 per cent hydrochloric acid for 3 hours on the water bath. The reducing value of the sugar formed was calculated as starch. Wood of birch, maple, alder, and elm collected in the spring showed no perceptible bluing with iodine-potassium iodide solution, but aspen and willow gave a strong starch coloration.

Storer,[4] using diastase, found the following amounts of starch:

	Inner wood, per cent	Outer wood, per cent	Bark, per cent
Gray birch felled in May	4.93	5.42	7.67
Gray birch felled in July	3.83	3.87	7.52
Gray birch felled in October	3.75	3.51	4.24
Sugar maple felled in October	1.94	2.43	5.97
Alder felled in January	....	3.04	

The starch content of the twigs of various trees has been determined microscopically[5] and polarimetrically after hydrolysis by heating with 1 per cent hydrochloric acid on the water bath for 15 minutes.[6]

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[1] A. Manaresi and M. Tonegutti, *l.c.*, p. 714.

[2] W. E. Tottingham and F. Gerhardt, *l.c.*

[3] E. Beckmann, *Chem. Centr.*, **II** (1915), 1208.

[4] F. H. Storer, *Bull. Bussey Inst.*, **2** (1897), 389.

[5] R. Lucks, *Landw. Jahrb.*, **53** (1919), 586–615.

[6] Von Wissel, *Landw. Jahrb.*, **53** (1919), 617–625.

Sugar.—Little information is available on the amount of sugar present in wood. Fischer[1] has made qualitative tests with Fehling's solution. The sap of the sugar maple contains an average of 3 per cent of sucrose. It has been calculated that the average sugar maple contains 135 gallons of sap or 35 pounds of sugar.[2]

The "sand" obtained in the manufacture of maple syrup contains 65 to 80 per cent of calcium malate and 6 to 18.5 per cent of silica.[3] In addition to malic acid, small amounts of *d*-tartaric acid and tricarballylic acid have been found.[4] It has been observed that in sunlight the crushed tissues of maple shoots can partially convert malic acid into sugar.[5]

PERCENTAGE OF AVAILABLE CARBOHYDRATE FOOD IN MAPLE WOOD

Determination	December, January, and February	March and April	May, June, July, and August	September, October, and November
Outer base wood:				
Water	35.01	32.86	30.30	29.80
Sucrose	0.94	0.80	0.36	0.72
Reducing sugars	1.40	0.53	0.13	0.41
Starch	0.78	0.96	1.01	1.43
Inner base wood:				
Water	30.28	29.64	26.87	29.05
Sucrose	0.49	0.52	0.18	0.41
Reducing sugars	0.65	0.33	0.09	0.26
Starch	0.43	0.49	0.62	0.51
Top wood (outer and inner):				
Water	33.85	31.36	32.46	32.14
Sucrose	1.12	1.04	0.41	0.83
Reducing sugars	1.79	0.67	0.23	0.59
Starch	1.09	1.33	1.23	1.63

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[1] A. FISCHER, *Jahrb. wiss. Botanik.*, **22** (1891), 73–160.

[2] VERMONT *Agr. Exp. Stat. Bull.*, **105** (1904).

[3] J. F. SNELL and A. G. LOCHHEAD, *J. Ind. Eng. Chem.*, **6** (1914), 301–302; W. H. WARREN, *J. Am. Chem. Soc.*, **33** (1911), 1205–1211.

[4] E. O. VON LIPPMANN, *Ber.*, **47** (1914), 3094–3095.

[5] W. R. BLOOR, *J. Am. Chem. Soc.*, **34** (1912), 534–539.

The amount of starch and sugars present in the wood of the sugar maple have been determined by Jones.[1] (See above Table.) The sugar content is highest in winter and lowest in summer. The sugar is practically limited to the sapwood, especially the outer layers. The per cent of sugar present based on the entire wood of the trunk would be exceedingly small.

Nitrogen.—The percentages given in the early analyses of wood are usually much too high. Most woods contain 0.1 to 0.3 per cent nitrogen (Tables 3 and 4). Tinkler[2] found 0.331 and 0.404 per cent nitrogen in various kinds of oak. Storer[3] found 0.10 to 0.156 per cent in fresh logwood and 0.141 to 0.164 per cent after leaching. The outer wood of a gray birch felled in October contained 0.52 per cent. According to Hartig,[4] nitrogen decreases during the fruiting period. Beech wood contained 0.098 to 0.392 per cent nitrogen and this decreased to 0.01 per cent during a year of heavy fruiting.

König[5] states that wood loses nitrogen by soaking in a solution of copper sulphate.

The nature of the nucleic acids in the protein of wood does not appear to have been investigated. Guerin[6] digested wood with 1 per cent potassium hydroxide for several days. The extract contained a nitrogenous compound of the following composition:

	Per Cent
C	52.762
H	5.040
S	0.666
P	4.600
Mn	0.402

The high manganese content is of interest. It appears to be combined in this manner in the woody tissues of all plants.

Nitrogen also occurs in wood in the form of alkaloids and other compounds. The wood of *Celtis reticulosa*, a large tree growing in the East Indies, contains indol and skatol; their origin is probably pathological.[1]

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[1] C. H. Jones, *J. Assoc. Official Agr. Chem.*, **2** (1916), 103–111.

[2] C. K. Tinkler, *Biochem. J.*, **15** (1921), 482.

[3] F. H. Storer, *Bull. Bussey Inst.*, **2** (1877–1900), 28.

[4] R. Hartig, *Botan. Zeit.*, **46** (1888), 837.

[5] R. König, *Chem. Centr.*, **32** (1861), 588.

[6] G. Guerin, *Compt. rend.*, **125** (1897), 311–312.

Secondary Constituents.—The secondary compounds occurring in wood are many and varied; they include gums, oleoresins, volatile oils, tannins, coloring matters, etc., some of which are of great economic importance.

A few woods are rich in tannins, while all appear to contain small amounts of these or related bodies. The tannins may be roughly divided into two groups, catechol and pyrogallol; the members of the former give a greenish-black coloration with ferric alum, and the latter a bluish-black. Moureau and Dufraisse[2] have observed that some phenols possess to a surprising degree the property of preventing oxidation; thus one molecule of hydroquinol will protect 40,000 molecules of acrylaldehyde from oxidation. Owing to the wide distribution of phenols in the vegetable kindgom, it is suggested that their function is to protect the plants from atmospheric oxidation.

Examination of the secondary constituents is in some cases an excellent means for distinguishing between species or varieties where the botanical differences are questionable. Schorger[3] examined the volatile oils from the oleoresins of *Pinus ponderosa* and *P. ponderosa scopulorum* and found that they were optically and chemically different. Henry and Flood[4] found differences in the composition of the oils from the needles of Douglas fir, *Pseudotsuga taxifolia*, and its variety *P. taxifolia glauca*.

Identification of woods by the character of the various extracts obtainable from them is capable of important development. Jauffret[5] has examined a large number of colored tropical woods and tabulated the following data: colorations obtained by treating the water and alcohol extracts with normal solutions of ferric chloride, sulphuric acid, sodium hydroxide, calcium hypochlorite, and sodium bisulphite; spectroscopic characteristics of the alcoholic (+NH_4OH) and aqueous (+NaOH) extracts. In most cases the chemical and spectroscopic properties of each species were distinct.

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[1] W. R. Dunstan, *Proc. Roy. Soc.*, **46** (1889), 211; C. A. Herter, *J. Biol. Chem.*, **5** (1909), 489–492.

[2] C. Moureau and C. Dufraisse, *Compt. rend.*, **174** (1922), 258–264.

[3] A. W. Schorger, *Proc. Soc. Am. Foresters*, **11** (1916), 33–39.

[4] A. Henry and M. G. Flood, *Proc. Roy. Irish Acad.*, **35B** (1920), 67–92.

[5] A. Jauffret, "La détermination des bois exotiques colorés d'après leurs caractères chimiques et spectroscopiques," Ann. Mus. Colonial de Marseille, [3] **8** (1920), 1–171.

Kanehira[1] has studied the fluorescence of the aqueous extracts of numerous species of American woods as an aid to identification.

Romanis[2] found that the resinous substances in fresh teak wood undergo a decided change with age. Advantage has been taken of this phenomenon to determine the degree of seasoning.[3] Steam distillation of fresh teak yields an oil, while crystals only are obtained from fully seasoned wood. The extent of seasoning can be determined by separating the oil from the crystals with methyl alcohol in which the latter are sparingly soluble.

Fat, Resin, and Wax.—It is a popular belief in the South that segregation of resin takes place in the stumps and fallen trunks of pines. This is erroneous. In actuality, the less resinous portions soon disappear through decay, leaving only the richer wood which is resistant. Nordenskjöld[4] found 15 to 22 per cent of resin in pine stumps that had stood for 10 years. The average resin content of 15 trees was 4.2 per cent for the sapwood and 15 per cent for the heartwood.

The resin content of some species used for paper making is given below:[5]

	Ether extract, per cent	Alcohol extract, per cent	Total extract, per cent
1. White spruce, seasoned	0.40	0.36	0.76
2. Black spruce, seasoned	0.24	0.36	0.60
3. Balsam, seasoned	0.85		
4. Balsam, green	1.20	1.35	2.55
5. Balsam, decayed	0.87	1.71	2.58
6. Jack pine, seasoned, large tree	2.70	0.99	3.69
7. Jack pine, green, small tree	3.24	1.71	4.95
8. Jack pine, rafted, seasoned	2.37	0.77	3.14

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[1] R. Kanehira, *J. Forestry*, **19** (1921), 736–739.

[2] R. Romanis, *J. Chem. Soc.*, **51** (1887), 868–871.

[3] A. C. Sircar, *J. Soc. Chem. Ind.*, **35** (1916), 452–454.

[4] I. Nordenskjöld, *Arkiv Kemi, Mineral. Geol.*, **4,** 28 (1912), 1–21.

[5] F. Barnes, *Chem. Met. Eng.*, **28** (1923), 504.

The following extractions were made on branches 2 to 4 years old.[1]

	Ether, per cent	Alcohol, per cent	Water, per cent	Total, per cent	Water only, per cent
Pinus silvestris, wood	7.87	4.19	3.55	15.61	6.62
Pinus silvestris, bark	19.58	14.76	13.27	47.61	28.50
Pinus abies, wood	4.40	2.12	2.45	8.97	4.96
Pinus abies, bark	10.66	14.22	13.43	38.31	21.95

Bergström[2] found that the soap obtained in cooking pine wood by the sulphate process consisted of a mixture of resin and fatty acids. Pine (*P. silvestris*) contained more fat than spruce (*Picea excelsa*). Fats are present only in winter, being converted into starch in spring. The heartwood is richest in resin and the sapwood in fats. The sapwood of pine felled in winter contained 0.3 to 1.5 per cent of fats. The fats consisted of the glycerides of oleic, linolenic, and palmitic acids, and contained a phytosterol (0.05 per cent), m.p. 133.5°, sparingly soluble in alcohol. Glycerine was detected in the ether-alcohol extract of the sapwood.

The following amounts of fat and resin are reported by Schwalbe:[3]

	Fat, per cent	Resin, per cent
Spruce, seasoned	0.50	0.48
Pine, seasoned	1.43	1.11

The fat consisted principally of the glyceride of oleic acid, with small amounts of the esters of linolic and linolenic acids.[4] The ether extract and alcohol extract of sulphite pulp contained 63 and 74 per cent respectively of fat. It is this fat which causes "resin spots" in paper[1] and "pitch trouble" on the paper machine.

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[1] O. Aschan and O. Rantalainen, *Brennstoff-Chemie,* **4** (1923), 101.

[2] H. Bergström, *Papier-Fabr. Fest u. Auslandsheft,* **9** (1911), 76–80; *Papier-Fabr.,* **11** (1913), 730.

[3] C. G. Schwalbe, *Forst u. Jagdwesen,* **47** (1915), 99.

[4] C. G. Schwalbe, *l.c.;* R. Sieber, *Z. angew. Chem.,* **29** (1916), 429.

The resins and fats change with age. Richter[2] found that as the wood seasoned, the ether extract decreased and the alcohol extract increased, though the latter was insufficient to balance the loss of ether extract. The acid and saponification numbers of the extractives increased with the aging of the wood, while the ester number decreased.[3] Oxidation promoted these changes.

The amount of resin and fat extractable from wood decreased from one-half to two-thirds through aging for 4 to 18 months.[4] The ether extract from pine wood was 6.3 per cent 6 days after comminution of the wood, and 2.1 per cent 127 days afterwards. An experiment with chips showed a reduction of the ether extract from 5.9 to 2.6 per cent in 15 days. The decrease in solubility is attributed to oxidation or condensation, or both. Without doubt the decrease is due to the formation of linoxyn, which is insoluble in most organic solvents and which retards solution of the resin.

Sawdust from Rafted Pine Wood

Days aged	Solvent	Extract, per cent	Resin, per cent	Fat, per cent
85	Ether	6.9	67.2	32.8
127	Ether	2.5	87.9	12.1
85	Benzene	7.3	75.8	24.2
127	Benzene	2.5	92.5	7.5

The amount of fat and resin in fresh and seasoned coniferous woods and in wood pulps has been extensively studied by Sieber.[5]

Walberg[6] found that drying the wood at 105° materially decreased the benzene extract but had no effect on the alcohol extract. Storage in air or nitrogen made no difference. Storage for 80 days showed no difference in resin content over a storage period of 10 days. The resin was very irregularly distributed in the wood and the statement of Mayr[1] that it occurs in largest amounts on the south side of the tree could not be confirmed.

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[1] C. G. Schwalbe, *Chem. Ztg.*, **38** (1914), 926.

[2] E. Richter, *Wochbl. Papierfabr.*, **44** (1913), 2486.

[3] C. G. Schwalbe and H. Grimm, *Wochbl. Papierfabr.*, **44** (1913), 3247.

[4] C. G. Schwalbe and W. Schulz, *Z. angew Chem.*, **31,** I (1918), 125–127; *Chem. Zeit.*, **42** (1918), 229–230.

[5] R. Sieber, "Harz der Nadelhölzer," *Schriften des Vereins der Zellstoff-u. Papierchemiker*, Berlin (1914), 109 pp.

[6] H. E. Wahlberg, *Papier-Fabr.*, **20** (1922), 1136.

Cutin.—The occurrence of cutin in wood is questionable. König and Rump[2] have reported 0.14 and 0.16 per cent of cutin in the crude fiber of beech and fir wood, respectively. The wood was freed from cellulose by treatment with 72 per cent sulphuric acid; the residue consisted of lignin and cutin from which the lignin was removed by oxidation with hydrogen peroxide and ammonia. Cutin is a wax containing 69 to 70 per cent carbon and 9 to 12 per cent hydrogen; saponification gives compounds agreeing with nonylic or capric acid, and cetyl or octadecyl alcohol. Of several woods examined by Dore,[3] oak alone gave a substance that might have been cutin.

Irritant Constituents.—Several species of wood contain compounds such as alkaloids, glucosides, and resins which irritate the skin and mucous membrane, and produce heart depression and paralysis of the motor centers. Workmen vary greatly in susceptibility. For this reason and the difficulty in isolating the active constituent or constituents in a pure state, there are contradictory reports on the physiological effects.

The active principle in East Indian satinwood (*Chloroxylon swietenia*) is the alkaloid chloroxylonine, $C_{22}H_{23}O_3N$; m.p. 182 to 183°.[4] Nestler[5] was unable to obtain irritation with either the wood or its extracts.

According to Nestler, liquid amber or red gum (*Liquidambar styraciflua* L.) from North America is not directly irritant, but the ether extract is strongly so. The alcohol, water, and chloroform extracts are inactive. The writer extracted an authentic sample of wood of this species with ether and obtained a solution with a green fluorescence. Application to the forearm of the brown, wax-like mass obtained on evaporation of the solvent did not produce a trace of inflammation after contact for 9 hours.

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[1] H. Mayr, "Das Harz der Nadelhölzer," Berlin (1894).

[2] J. König and E. Rump, "Chemie und Struktur der Pflanzen-Zellmembran," (1914), p. 52; *Z. Unters. Nakr. Genussm.*, **28** (1914), 177–222; *cf.* W. Suthoff, *Ibid.*, **17** (1909), 662–663.

[3] W. H. Dore, *J. Ind. Eng. Chem.*, **11** (1919), 556.

[4] S. J. M. Auld, *J. Chem. Soc.*, **95** (1909), 964–968.

[5] A. Nestler, *Ber. botan. Ges.*, **29** (1911), 672.

The irritant action of various species of cocobolo (*Dalbergia*) is apparently due to an oil.[1] Nestler[2] states that the active substance is soluble in water, but more easily in alcohol and benzene.

The species given in the table below have been examined by Matthes and Schreiber.[3] Lapachol and lapachonone are not irritant. Wood containing lapachol shows small cherry-red spots when moistened with 0.1*N* alcoholic potash. Lapachonone gives an intense indigo-blue solution with sulphuric acid. According to Baker,[4] wasahba wood, which is used for fishing rods, contains a resinous substance giving a red color with alkalis. It is about as sensitive as phenolphthalein. The resin may contain lapachol.

Species	Active principle	Compounds identified
Surinam greenheart (*Bignonia lucoxylon*)...................	Resin	Lapachol,[1] $C_{29}H_{26}O_4$
Guiana greenheart (*Nectandra rodiaei*)......................	....	(Lapachol absent)
Moah wood, East Indies (*Illipe longifolia*)..................	Resin	Lapachol; lapachonone
Teak (*Tectonia grandis*).........	Resin	
Native teak, Australia (*Flindersia australis*).	(Not toxic)	Flindersin, $C_{23}H_{26}O_7N_2$, an alkaloid; resin; oil
Lapacho wood, South America (*Bignoniaceæ*)...............	Resin	Lapachol
Tecoma araliacea...............	Resin	Lapachol

[1] C. A. Oesterle, *Arch. Pharm.*, **254** (1916), 346.

Other species reputed to possess irritant properties are: boxwood (*Buxus sempervirens* and *B. macowani*); African boxwood (*Gonioma kamassi*); satinwood (*Zanthoxylon flava*); green ebony (*Brya ebenus*); West Indian sabicu wood (*Lysiloma sabicu*); ebony, Borneo rosewood; magneta rosewood; olive wood; and mahogany.[5]

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[1] G. H. Garratt, *J. Forestry*, **20** (1922), 479.

[2] A. Nestler, *Ber. botan. Ges.*, **29** (1911), 672.

[3] H. Matthes and E. Schreiber, *Ber. botan. Ges.*, **24** (1914), 385–444; contains an extensive medical bibliography.

[4] G. B. Baker, *Chem. News*, **116** (1917), 139.

[5] G. H. Garratt, *J. Forestry*, **20** (1922) 479–487.

CHAPTER III

LIGNIN

Lignin represents the non-carbohydrate portion of lignified tissue after it has been freed from tannins, resins, fats, and similar secondary constituents. The study of lignin is rendered exceedingly difficult owing to the impossibility of isolating it unchanged. Furthermore, it is not uniform. There is a great difference in the methoxyl and acetyl contents of lignin from various species of woods, particularly between hardwoods and softwoods. Some variation exists even in lignin from different portions of the same tree. Lignin is easily oxidized by nitric acid. Halogens produce oxidation and substitution, the halogenated product being readily soluble in alkalis. It is soluble in acetyl bromide in the cold and in alkalis, sulphurous acid, and sulphite solutions at high temperatures. Treatment of lignified tissue with strong mineral acids, which dissolve the carbohydrates, leaves a residue of lignin.

The structure of lignin is still uncertain. In many of its reactions lignin closely resembles the tannins, though no convincing evidence of a cyclic structure has been produced. Pyrolytic methods are useless as a means of determining constitution. Nitration, chlorination, sulphonation, oxidation, and reduction give either indefinite products, or substances furnishing only questionable information on structure. Furan, benzofuran, pyrone, benzenoid, and aliphatic structures have been proposed. It has been definitely established that lignin contains methoxyl, acetyl, and hydroxyl groups, but the presence of ketonic and aldehydic groups has not been satisfactorily proved.

The hydroxyl groups, combined for the most part as esters and ethers, appear to be both phenolic and alcoholic. Assuming for the lignin of wood a nucleus of the order of C_{45}, it contains eight to ten hydroxyl groups, of which three to five are combined as methyl ethers, while the remainder are mostly acetylated.

One aldehydic and two ketonic groups may be present. The presence of formyl and carboxyl groups is doubtful.

The name lignin, in the sense in which we at present use it, appears to have been first employed by F. Schulze[1] in 1857. He, though not the first to do so, distinguished cellulose from lignin or incrusting matter by its resistance to oxidizing agents. By indirect analysis, lignin was assigned the formula $C_{38}H_{24}O_{20}$ and considered to be a pure material.

Dragendorff[2] in his classic work states that the vasculose of Fremy agrees in the main with his lignin. He mentions that lignin cannot be separated from cellulose without decomposition, so that it is impossible to obtain direct proof whether it consists of one or several chemical individuals. On the basis of the work of his students, he is inclined to the opinion that cellulose is associated with a single definite substance, lignin. Several species of wood were examined by Stackmann;[3] after exhaustion with neutral solvents, dilute alkali and acid, the composition of the lignin was determined by ultimate analysis of the purified material before and after treatment with chlorine. The lignin of dicotyledons contained:

	Per Cent
C	53.1–59.6
H	4.4– 6.3
O	34.1–38.9

The results are subject to correction for "wood gum" that had not been discovered.

Schuppe[4] found from 3.25 to 7.09 per cent of wood gum in various angiosperms, and by making the necessary deductions obtained for most woods about 17 per cent of lignin. Wood was treated with water, alcohol, and dilute sodium hydroxide, and analyzed. He proposed for lignin the formula $C_{19}H_{18}O_8$, and for wood $5C_6H_{10}O_5 + C_{19}H_{18}O_8$.

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[1] F. Schulze, *Chem. Centr.*, **28** (1857), 321–325. Czapek ("Biochemie d. Pflanzen," vol. I (1913), p. 682), without giving a reference, credits de Candolle with priority in the use of lignin. A. de Candolle in his "Organographie Vegetale," Paris (1827), and "Introduction a l'Etude de la Botanique," Paris (1835), uses the terms *couches ligneuses*, *portion ligneuse*, and *corps ligneux* in the sense of Malpighi and other earlier writers as representing the woody portion of the tree.

[2] G. Dragendorff, "Plant Analysis," London (1884).

[3] Stackmann, "Studien über die Zusammensetzung des Holzes," Diss. Dorpat (1878).

[4] N. Schuppe, "Beiträge zur Chemie des Holzgewebes," Diss. Dorpat (1882).

	Lignin, Per Cent	Wood, Per Cent
C	60.56	45.4
H	4.66	5.9
O	34.80	48.7

In 1889, Cross and Bevan[1] advanced an empirical formula for jute lignocellulose and formulated its reaction with chlorine. The equation does not balance, but the chlorine derivative of lignin was assigned the formula $C_{19}H_{17}Cl_4O_9$. Later[2] the compound was given as $C_{19}H_{18}Cl_4O_9$, containing uniformly 26.7 per cent of chlorine, the parent substance being $C_{19}H_{22}O_9$.

Lignin appears to be profoundly modified by all methods employed for its isolation; hence it seems best to group the literature for the most part under the process whereby the lignin was obtained.

Lignin Isolated with Sulphite Solutions.—The industrial importance of the sulphite process for pulping wood has led to an extensive investigation of the constitution of lignin through a study of the reaction whereby the lignin is dissolved. Lindsey and Tollens[3] used a waste sulphite liquor obtained by cooking coniferous wood by the Ritter-Kellner process. Lead acetate gave a precipitate which on decomposition with sulphuric acid and precipitation with alcohol had the empirical composition $C_{26}H_{30}SO_{12}$. The filtrate on evaporation gave a gummy compound $C_{26}H_{30}SO_{12}$. When the original liquor was treated with bromine, the derivative, $C_{26}H_{28}Br_4SO_{11}$, was thrown down, while with hydrochloric acid the precipitate was represented by $C_{26}H_{30}SO_{10}$. Distillation with hydriodic acid showed the presence of two methoxyl groups. The sulphur was present as $-SO_3H$. It was concluded that the ligneous body had the composition $C_{24}H_{24}(OCH_3)_2O_{10}$ or $C_{24}H_{26}(OCH_3)_2O_{10}$. Fractional precipitation of sulphite liquor with alcohol by Seidel[4] failed to produce constitutional differences in the precipitates. A carefully purified fraction had the composition C, 56.27 per cent; H, 5.87 per cent; and S, 5.52 per cent. This analysis corresponds closely with the formula $C_{26}H_{30}SO_{12}$ of Lindsey and Tollens.

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[1] C. F. Cross and E. J. Bevan, *J. Chem. Soc.*, **55** (1889), 207.

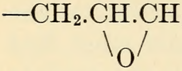
[2] "Researches" (1895–1900), pp. 126, 134.

[3] J. B. Lindsey and B. Tollens, *Ann.*, **267** (1892), 341.

[4] H. Seidel, *Mitt. k.k. techn. Gewerbe-Mus.*, **7** (1897), 219.

When sulphite liquor was treated with bleaching powder in the presence of hydrochloric acid, a chlorine derivative was obtained, which, after purification with alcohol and ether, had the composition $C_{26}H_{29}ClSO_{12}$.[1] Streeb[2] obtained the formula $C_{18}H_{24}SO_{10}$ for ligninsulphonic acid from sulphite liquor.

To isolate the lignin from sulphite liquor, Klason[3] heated the latter with calcium chloride whereby about half of the calcium salts of lignin was precipitated. Purification was effected by treating the salts with sulphuric acid, and then with alcohol to throw down the calcium sulphate. After evaporation of the alcohol from the filtrate, the free sulphonic acids were taken up in water, neutralized with barium hydroxide, and the barium salt precipitated with alcohol. Analysis of the salt showed the composition $C_{40}H_{44}O_{17}S_2Ba$. The molecular weight was about 6,000, so that lignin would be expressed by the formula $(C_{40}H_{42}O_{11})_6$. The purified salt gave none of the lignin color reactions. It contained 11.5 per cent methoxyl, corresponding to $4CH_3O$ for each C_{40}. Treatment of the calcium salt with *p*-bromobenzoylchloride pointed to the presence of one hydroxyl group. It did not condense with phenylhydrazine or benzylphenylhydrazine; however, some evidence of the presence of an active carbonyl group was drawn from heating the ligninsulphonic salt with calcium bisulphite solution whereby a loose combination with two molecules of SO_2 was obtained. The presence of an ethylene linkage was shown by the addition of a molecule of iodine.

Klason advanced the hypothesis that lignin consists of a condensation product of coniferyl and oxyconiferyl alcohol. Coniferyl alcohol is resinified readily by mineral acids, as is lignin, when a sulphite cook is deficient in lime. Lignin combines with four molecules of SO_2, two of which are present in the form of the sulphonic acid. The third is more loosely combined and, although not titratable with iodine, gradually splits off as sulphuric acid on standing in the air. The fourth molecule is the most weakly combined and can be titrated with iodine. Since the salt $C_{40}H_{44}O_{17}S_2Ba$ can combine with only two atoms of iodine, an active carbonyl group must be present as a glycide,  $-\underset{\diagdown O \diagup}{CH_2.CH.CH_2}$, as it does not react with phenylhydrazine but does with sulphur dioxide. A $-CH_2.CO.CH_3$ group is not present, since no acetic acid is formed by oxidation with nitric acid. It is assumed that in each C_{40} group there are present four CH_3O and three OH groups. Experimental evidence indicated only one or two hydroxyl groups, but it is probable that a $-C.COH$ group passes to $-CH.CO-$. Since the lignin isolated directly from spruce contained 7.01 per cent methyl corresponding with two CH_3O groups and the salt $C_{40}H_{44}O_{17}S_2Ba$ contained four CH_3O groups, there must be at least two forms of lignin in sulphite liquor, that not precipitated by calcium chloride being practically free from methoxyl. There is considerable analogy between lignin and the tannins; in fact, lignin may be considered as an insoluble tannin, the side groups being in the 1, 3, 4, and 5 position, as in gallic acid, thereby explaining its ready oxidizability.

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[1] H. Krause, *Chem. Ind.*, **29** (1906), 217.

[2] E. Streeb, "Ueber Derivate des Lignin's," Diss. Göttingen (1892), 31 pp.

[3] P. Klason, "Zusammensetzung des Fichtenholzes" (1910), p. 15.

In subsequent papers, Klason's hypothesis of the composition and constitution of lignin has undergone many modifications. In 1916, lignin was formed as follows:[1]

$$\underset{\text{Coniferyl alcohol}}{1C_{10}H_{12}O_3} + \underset{\text{Oxyconiferyl alcohol}}{3C_{10}H_{12}O_4} + \underset{\text{Trioxycinnamyl alcohol}}{6C_9H_{10}O_4} = \underset{\text{Lignin}}{C_{94}H_{88}O_{29}} + 10H_2O.$$

The lignin precipitated from sulphite liquor with calcium chloride in the form of calcium ligninsulphonate has the formula $C_{40}H_{40}O_{11}$, and that remaining in solution, $C_{54}H_{48}O_{18}$.

The calcium salt of ligninsulphonic acid precipitated by calcium chloride is formed as follows:[2]

$$\underset{\text{Coniferyl alcohol}}{1C_{10}H_{12}O_3} + \underset{\text{Oxyconiferyl alcohol}}{3C_{10}H_{12}O_4} + 1Ca(SO_3H)_2 = C_{40}H_{44}O_{18}S_2Ca + 3H_2O.$$

This corresponds with the formula $C_{40}H_{42}O_{12}$ with four CH_3O groups. The calcium salt reacts with napthylamine to give a yellow precipitate. With the salt not precipitated by calcium chloride there is obtained the compound $C_{59}H_{66}O_{17}S_2N_3$. It may be formed as follows:

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[1] P. Klason, *Svensk Papers-Tid.*, **17** (1916); *Arkiv Kemi, Mineral. Geol.*, **6**, 15 (1917), 6.

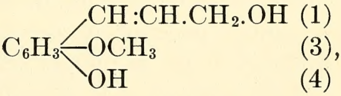
[2] P. Klason, *Arkiv Kemi, Mineral. Geol.*, **6**, 15 (1917), 1–21.

$$1\underset{\text{Coniferyl alcohol}}{C_{10}H_{12}O_3} + 1\underset{\text{Oxyconiferyl alcohol}}{C_{10}H_{12}O_4} + 1\underset{\text{Caffeic acid}}{C_9H_8O_4} + 2\underset{\text{Sulphurous acid}}{H_2SO_3} + 3\underset{\text{Napthylamine}}{C_{10}H_9N} = C_{59}H_{57}O_{14}S_2N_3\text{[1]} + 3H_2O.$$

This compound corresponds with the formula $C_{29}H_{26}O_8$, so that the total lignin has the formula $C_{69}H_{68}O_{20}$ with six CH_3O groups. Klason believes that the lignin of fir is formed by condensation of oxy and methylated derivatives of cinnamic alcohol and related aldehydes and acids.

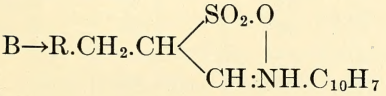
On reviewing the paper, the impression is gained that compounds were chosen in such a way that they could be condensed to fit the empirical formula obtained on analysis, rather than on the basis of experimental evidence. The fact that wood on oxidation with ozone[2] does not give vanillin or one of its derivatives is a strong indication that lignin does not contain a coniferyl alcohol group.

The β-napthylamine ligninsulphonate obtained from the calcium salt precipitated with calcium chloride exists in two forms, thus supporting, according to Klason,[3] the theory that lignin has a constitution similar to coniferyl alcohol,



$$C_6H_3\left<\begin{array}{ll} CH{:}CH.CH_2.OH & (1)\\ OCH_3 & (3),\\ OH & (4)\end{array}\right.$$

which is a substituted allyl alcohol. A part of the allyl alcohol complex exists in the form of the aldehyde and this reacts with sulphurous acid and napthylamine as follows:

1. $R.CH{:}CH.CHO + H.SO_2.OH = R.CH_2.CH(SO_2.OH).CHO$ (A).
2. $A + C_{10}H_7NH_2 = R.CH_2.CH(SO_2.O.NH_3.C_{10}H_7)CHO$ (B).
3.  (C).

$$B \rightarrow R.CH_2.CH\left<\begin{array}{l} SO_2.O\\ \quad | \\ CH{:}NH.C_{10}H_7\end{array}\right.$$

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[1] Owing to the use of an incorrect formula ($C_{10}H_{10}N$) for napthylamine in the original (p. 7), the compound is stated to be $C_{59}H_{60}O_{14}S_2N_3$ and the combustion figures compared with this formula.

[2] C. Dorée and M. Cunningham, *J. Chem. Soc.*, **103** (1913), 677.

[3] P. Klason, *Ber.*, **53** (1920), 706–711; 1862–1863; **55** (1922), 448.

The white precipitate B first obtained rearranges in acid solution to give the intense yellow cyclic salt C. The positions 1, 3, and 4 are based on the rather slender evidence furnished by the presence of vanillin in sulphite liquor and the formation of *n*-propyl creosol by the destructive distillation of wood. The napthylamine salts prepared from the sulphite liquor in which various woods were cooked had fundamentally the same appearance and properties as that from fir. Their composition is shown below:

	Spruce, per cent	Pine, per cent	Birch, per cent	Oak, per cent	Aspen, per cent	Willow, per cent	Beech, per cent
N	2.07	1.95	2.40	1.82	1.87	2.04	2.00
S	5.22	5.34	4.84	5.02	4.84	5.43	5.26

Hintikka[1] considers untenable the belief that there occurs in lignin an acrolein group which combines with bisulphites to form a sulphonic acid giving the yellow cyclic salt C. The difference in behavior of the salts B and C on treatment with dilute caustic soda as reported by Klason could not be substantiated. It is apparently a simple salt.[2]

The lignin of spruce wood exists in two forms,[3] 63 per cent being acrolein- or α-lignin, and 37 per cent carboxyl- or β-lignin. α-Lignin contains an acrolein group in the form of coniferyl aldehyde. Its sulphonic acid forms cyclic aryl ammonium salts and its calcium salt is precipitated by calcium chloride. The calcium salt has the composition:

		Calculated	Found
C_{40}	480	52.41	52.82
H_{44}	44	4.79	5.08
O_{18}	288	31.45	
S_2	64	6.98	6.58
Ca	40	4.37	4.15
	916	100.00	
$4CH_3O$	124	13.53	12.19

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[1] S. V. Hintikka, *Cellulosechemie*, **2** (1921), 63; **4** (1923), 93.

[2] C. Dorée and L. Hall, *J. Soc. Chem. Ind.*, **43** (1924), 261T.

[3] P. Klason, *Ber.*, **53** (1920), 1864–1873.

Klason believes that the above formula should be cut in half. Furthermore, it is subject to a correction, for the acetic acid split off during heating with sulphite liquor. When 45 grams of wood were cooked with sulphite liquor until all the lignin had been removed, 0.945 gram of acetic acid was formed, while subsequent hydrolysis with sulphuric acid yielded an additional 0.21 gram. Of the total 1.155 grams of acid, 10 per cent consisted of formic acid. Spruce wood digested with N H_2SO_4 on the water bath for 24 hours gave 2.1 per cent acetic acid. Assuming the presence of one acetyl group, and that α-lignin constitutes about 63 per cent of the total lignin (30 per cent), the theoretical yield would be 2.86 per cent of acetic acid. The corrected formula for α-lignin would be $C_{22}H_{22}O_7$, having probably the constitution of a flavone. The hydroxyl groups in α-lignin are either methylated or acetylated.

β-Lignin contains an acrylic acid group R.CH:CH.COOH and has the formula $C_{19}H_{18}O_9$. According to calculation, the wood should give 3.78 per cent CH_3O, when actually 4.1 per cent was found. This is attributed to the formation of some ethyl iodide from the complex $R.CH{:}CH.CH_2OH$. Coniferin gave 9.73 per cent CH_3O against the calculated 8.20 per cent. It has been shown, however, that methoxyl is the sole alkoxyl group in wood and lignin.[1]

Further analyses of the β-naphthylamine and calcium salts of β-ligninsulphonic acid indicate the formula $C_{19}H_{18}O_7$ instead of $C_{19}H_{18}O_9$. β-Lignin may be formed by condensation of one molecule of coniferyl aldehyde with one molecule of caffeic acid.[2]

Spruce wood after extraction with ether to remove resins was extracted alternately with water and alcohol, which removed 12 per cent of the weight of the wood.[3] The residue from evaporation of the alcohol extract was extracted with chloroform; the soluble portion contained 66.14 per cent C, and 6.49 per cent H; the insoluble portion 59.97 per cent C, and 5.66 per cent H. The first substance on oxidation gave a vanillin odor and was considered from analyses and molecular-weight determinations to be in good agreement with coniferyl alcohol, $C_{10}H_{12}O_3$;

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[1] E. Hägglund and B. Sundroos, *Biochem. Z.*, **146** (1924), 221.

[2] P. Klason, *Ber.*, **56** (1923), 300.

[3] P. Klason, "Zusammensetzung des Fichtenholzes," p. 30.

while the second was a dimeric form, $(C_{10}H_{12}O_4)_2$, of oxyconiferyl alcohol. The portion insoluble in chloroform when completely freed from water by heating at 130° contained 63.94 per cent C and 5.74 per cent H.[1] Since about 65 per cent combines with β-napthylamine the product giving the typical reactions for lignin contains two-thirds α-lignin and one-third β-lignin. The lignin thus extracted directly from wood is substantially in agreement with the lignin obtained from sulphite liquor. Lignin and its sulphonic acid appear to be optically inactive.

The homogeneity of calcium α-ligninsulphonate was shown by the uniformity of the analyses of the β-napthylamine salts obtained by: treating waste sulphite liquor with calcium chloride; fractional precipitation of the waste liquor with sodium chloride; and from the portion remaining dissolved.[2] When α-ligninsulphonic acid is oxidized with hydrogen peroxide, α-napthylamine precipitates a salt, $C_{40}H_{38}O_{11}SN_2$.

$$C_{20}H_{20}O_6 + H_2SO_3 + 2C_{10}H_7.NH_2 + O_2 - H_2 = C_{40}H_{38}O_{11}SN_2.$$

	C	H	S	N
Calculated	63.64	5.08	4.25	3.71
Found	63.29	5.33	4.20	3.49

It is concluded from the composition of the salt that an aldehydic group has been oxidized to a carboxyl group and a methylene group to a ketonic group. The presence of two hydroxyl groups is shown by the preparation of a diacetyl derivative of β-napthylamine-α-ligninsulphonate; however, since only one group can be methylated, one is probably attached to a benzenoid nucleus, the other to an aliphatic group.

The flavone structure proposed for α-lignin has been abandoned in favor of the following formula,[3] which contains a benzofuran ring. This structure explains the formation, on destructive distillation, of guaiacol, catechol, *m*- and *p*-cresols, methyl-, ethyl-, and

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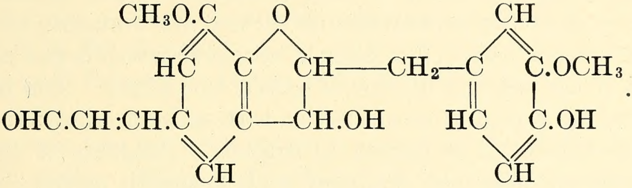
[1] P. Klason, *Ber.*, **55** (1922), 455–456.

[2] P. Klason, *Ber.*, **55** (1922), 448–455; *Svensk Kem. Tid.*, **34** (1922), 4–17.

[3] P. Klason, *Ber.*, **56** (1923), 300.

n-propylcreosols, methyl alcohol, allyl alcohol, and 2-methylfuran. It has been shown that α-lignin is a chemical compound in which can be quantitatively determined an acrolein group, two methoxyl groups, a phenolic and alcoholic hydroxyl group, an aliphatic methylene group, and oxidic oxygen. A body of the above constitution must show two aromatic nuclei connected by a cumarone or furan ring. Klason also points out the close relationship of the above formula to gambier-catechu, 2.4.6.3′.4′ -pentamethoxy-α, γ-diphenylpropane, synthesized by Freudenberg,[1] in view of the opinion held by many investigators of the similarity of lignin to the tannins.



An apparently close relationship exists between certain alcohol-soluble resins, tannins, and lignin.[2] Spruce needles gave with 95 per cent methyl alcohol an extract separable into three main fractions, a crude fat soluble in ether, a crude resin insoluble in ether but soluble in alcohol, and a syrup soluble in water. The three fractions contained bodies derived from hydroxycinnamic acids, aldehydes, and alcohols, that differed from each other in various degrees of methylation, hydroxylation, hydrogenation, and condensation. The crude fat contained 29 per cent of abiephyllic acid having the properties of a tannin. The crude resin contained bodies having aldehydic and ketonic properties and behaving like a tannin in that an alcoholic solution precipitates gelatin, and an alkaline solution on acidification precipitates a "red" similar to the phlobaphenes.

The crude resin resembles the α-lignin and the water-soluble syrup the β-lignin of Klason. A closely related series of tannic acids isolated from the syrup represents ketoacids derived from hydroxycinnamic acid and related to *p*-cumarylferulic acid or feruylferulic acid, and to caffeic acid. Coniferous wood, after a preliminary extraction with benzene, yields to alcohol a resin considered to be a soluble form of lignin.[1] In view of the presence of various cinnamic acid derivatives in the resin of *Pinus laricio*,[2] it may be questioned whether there is any genetic relationship between these substances and lignin.

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[1] K. Freudenberg, *Ber.*, **53** (1920), 1416.

[2] A. C. von Euler, *Cellulosechemie*, **2** (1921), 128–135; **3** (1922), 1–7.

When sulphite liquor is heated at 60 to 70° with 21 per cent of its weight of sodium chloride, β-lignin-S-acid remains in solution while α-lignin-S-acid is precipitated.[3] The latter differs materially from Klason's ligninsulphonic acid obtained by precipitation with $CaCl_2$. The α-lignin-S-acid is a mixture of ligninsulphonic acids of high molecular weight (about 900); since conductivity measurements showed one ionizable hydrogen atom for each atom of sulphur, a carboxyl group is not present. Most of the sulphur dioxide is loosely combined. The product purified by repeated precipitation with sodium chloride showed no constant ratio of carbon to sulphur. Products of constant composition were not obtained with aromatic amines; as one nitrogen was present for each sulphur atom, the acidity is entirely due to the sulphur group. The composition of the sulphur-free compound varied from $C_{28}H_{34}O_8$ to $C_{34}H_{44}O_{11}$. Since acetic acid is split off by alkalis, α-lignin may consist of a mixture of substances differing from a parent substance in the wood through the loss of formyl and acetyl groups.

Holmberg[4] on extracting a liter of sulphite liquor with ether obtained 0.2 gram of a lactone, $C_{20}H_{20}O_6$, called sulphite liquor lactone. It crystallizes in plates or prisms and melts at 250 to 255°. In alcoholic solution it gives with ferric chloride a green coloration changing to brown; with phloroglucinol and hydrochloric acid there is no reaction, but an alkaline solution of the lactone after exposure to air gives an intense cherry-red coloration with this reagent. Ligninsulphonic acids from sulphite liquor exhibit a similar behavior. The lactone is presumably that of diguaiacyltetramethylene-carbinol carboxylic acid:

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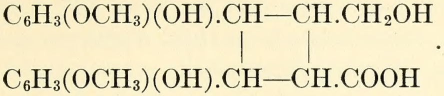
[1] A. C. von Euler, *Cellulosechemie*, **4** (1923), 4.

[2] M. Bamberger, *Monatsh.*, **12** (1891), 445; **15** (1894), 505.

[3] K. H. A. Melander, *Cellulosechemie*, **2** (1921), 41–43, 69–73; *J. Soc. Chem. Ind.*, **38** (1919), 625A.

[4] B. Holmberg, *Svensk Kem. Tid.*, **32** (1920), 56–67; *Ber.*, **54** (1921), 2389–2406.



$$\begin{array}{l} C_6H_3(OCH_3)(OH).CH\text{—}CH.CH_2OH \\ \qquad\qquad\qquad\qquad\quad | \qquad\; | \\ C_6H_3(OCH_3)(OH).CH\text{—}CH.COOH \end{array} .$$

Sulphonation of the lactone and subsequent treatment with water yields a monosulphonic acid, m.p. 172 to 173°. Dimethylsulphate gives α-dimethyl-sulphite-liquor-lactone, $C_{18}H_{12}O_2.(OCH_3)_4$, in the form of silky needles, m.p. 179 to 180°; $[\alpha]_D^{18°} = -100.9°$. The α-compound on treatment with sodium ethoxide gives an inactive β-dimethyllactone.[1]

The lactone is found in greater quantity in the first part of the period of the digestion of spruce wood with sulphite liquor than towards the end.[2] It was not obtained from spruce bark or pine wood.

No success has yet been attained in isolating definite lignin-sulphonic acids. Hönig and Spitzer,[3] by the fractional precipitation with alcohol of the calcium or barium salts from evaporated sulphite liquor, obtained fractions of variable composition roughly divisible into three classes: (1) $C_{43}H_{50}O_{18}S_2Ba$, containing four CH_3O groups; (2) $C_{40}H_{44}O_{18}S_2Ba$, containing one CH_3O group; and (3) $C_{74}H_{114}O_{48}S_2Ba$, containing three CH_3O groups, and representing the portion remaining unprecipitated by alcohol. The salts on ultimate analysis showed the following composition:

	(1) per cent	(2) per cent	(3) per cent
C	49.39	47.41	44.43
H	4.75	4.96	5.75
S	6.39	6.46	3.65
Ba	10.81	11.29	6.90
CH_3O	11.15	2.95	4.86

It is conceivable that salt 2 is formed from salt 1 by elimination of three methoxyl groups. The free lignin acids were soluble in water, glacial acetic acid, and alcohol, and liberated carbon dioxide from carbonates and acetic acid from acetates. In their opinion, though the ligninsulphonic acids so far isolated are not uniform substances but mixtures, the several sulphonic acids are best characterized by their methoxyl content.

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[1] B. Holmberg and M. Sjöberg, *Ber.*, **54** (1921), 2406–2407.

[2] S. V. Hintikka, *Cellulosechemie*, **4** (1923), 93.

[3] M. Hönig and J. Spitzer, *Monatsh.*, **39** (1918), 1–14.

McKee and Barsky[1] fractionally precipitated the calcium salts of ligninsulphonic acids from sulphite liquor, later converting them into the barium salts by Klason's method, and obtained fractions of very variable composition. The carbon content varied from 59.7 to 55.1 per cent and the hydrogen from 6.4 to 5.9 per cent.

König[2] isolated a barium ligninsulphonate of the composition $C_{46}H_{40}O_{27}S_2Ba$ by spraying concentrated sulphite liquor into 50 per cent sulphuric acid, neutralizing the precipitated ligninsulphonic acid with barium carbonate, and precipitating the resulting salt with alcohol. Colorless products were not obtained, due to some decomposition. Ligninsulphonic is probably dibasic, shows a high degree of ionization, and must be classed as a strong acid. On the other hand, solutions of barium ligninsulphonate even in great dilution are optically non-homogeneous, a part of the salt being, accordingly, in colloidal solution. In the salt solution, two systems of equilibrium coexist: Colloid $\rightleftarrows$ Simple Molecules; Molecules $\rightleftarrows$ Ions; with increasing dilution both systems shift from left to right. The barium salt showed a molecular weight of 1110 from the freezing-point depression of an aqueous solution. Reduction of the salt with sodium and alcohol gave no definite products. With palladium and hydrogen 1.7470 grams of the barium salt took up 43.0 cubic centimeters of hydrogen, showing the presence of one reducible double bond to two atoms of sulphur, on the assumption that the reduction of an aldehyde group does not take place.

By the action of sulphurous acid on spruce wood there is obtained a ligninsulphonic acid which, after purification by dialysis, behaves as a homogeneous substance of the formula $C_{26}H_{30}O_{12}S$.[3] Its various reactions indicate the presence of the groupings $C_{21}H_{15}O_2.(SO_3H).(OH)_2.(CH_2OH).(CHOH).(CHO)$.-

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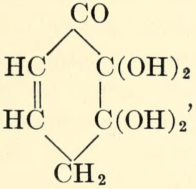
[1] R. H. McKee and G. Barsky, *Paper Trade J.*, **74,** 20 (1922), 46–48.

[2] F. König, *Cellulosechemie*, **2** (1921), 93–103, 105–113.

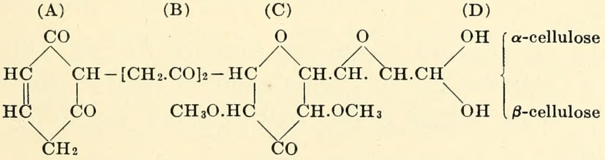
[3] C. Dorée and L. Hall, *J. Soc. Chem. Ind.*, **43** (1924), 257–263T.

$(OCH_3)_2$. The nitrated product does not behave as the nitro-derivative of a phenol, but of a non-benzenoid body of the nature of the terpenes. Oxidation with nitric acid of a concentration of 32 per cent gives oxalic acid and the acid $C_{20}H_{24}O_{12}.(COOH)_6.(NO_2)_2$. The continuance of the C_{26} unit and the stability of a C_{20} nucleus throughout the various reactions lend support to Schrauth's[1] view that lignin is related to a reduced benzophenanthrene hydrocarbon.

Cross and Bevan's Formula for Lignin.—The chlorine derivative of lignin, $C_{19}H_{18}Cl_4O_9$, called lignone chloride by Cross and Bevan,[2] is given a ketonic character. Its constitution is similar to the chlorine derivatives of pyrogallol, namely, mairogallol, and leucogallol, derived from  , the general type, and linked by oxygen bonds into three C_6 complexes.[3]

Lignone chloride on heating gave a slight sublimate of chloroquinone and on reduction yielded trichloropyrogallol, the identifications being based on color reactions. Lignone chloride and the chlorine derivatives of pryogallol gave identical color reactions with sodium sulphite and ferric chloride.

The above formula was subsequently elaborated to conform with additional experimental data on the behavior of the lignone complex and its relationship to α- and β-cellulose.[4]



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[1] W. Schrauth, *Z. angew. Chem.*, **36** (1923), 149; *Ber.*, **57** (1924), 854.

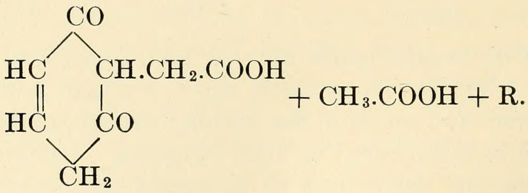
[2] C. F. Cross and E. J. Bevan, "Cellulose" (1895), p. 136.

[3] A. Hantzsch and K. Schniter, *Ber.*, **20** (1897), 2033.

[4] "Researches" (1905–1914), p. 104; C. F. Cross, "Lectures on Celulose" (1912).

In the benzenoid group A, chlorination takes place at the ethylene and CH_2 positions to form a quinone chloride. With jute, combination with chlorine is one of substitution and addition, since the lignone chloride contains uniformly 26.7 per cent chlorine, and the chlorine as HCl is one-half of that combined.[1] The above structure would, however, give a lignin, as the aldehyde, of the formula $C_{20}H_{22}O_{10}$ and not $C_{19}H_{22}O_9$,[2] by the elimination of a molecule of water. The presence of a ketene group B explains the formation of acetic acid by hydrolysis, oxidation, and destructive distillation. The occurrence of a pyrone or hydropyrone group C is based on the production of acetone and maltol at elevated temperatures; while the reaction of lignocellulose with bisulphites and the formation of ligninsulphonates are due to the aldehyde group D.

The formula proposed for lignin may be looked upon as a substituted diketide, which on hydrolysis at B would give the ketonic form of a dihydroxyphenylacetic acid.



The evidence for the presence of a pyrone ring is not particularly strong. The small amount of acetone obtainable on destructive distillation could be formed by secondary decomposition of acetic acid, while maltol is also obtained in the distillation of cellulose.[3]

Equally satisfactory theoretical formulæ for the constituent groups of Cross and Bevan's lignin might be derived from ketene, $CH_2{:}CO$, alone, owing to the extraordinary reactivity of this compound.

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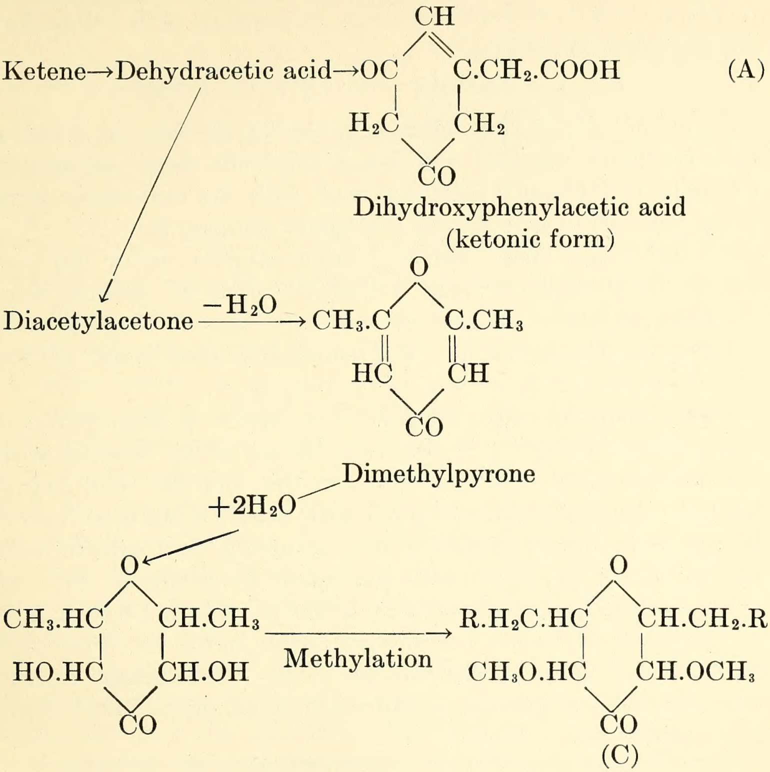
[1] "Cellulose" (1916), p. 104.

[2] "Researches" (1905–1910), p. 103.

[3] E. Erdmann and C. Schaefer, *Ber.*, **43** (1910), 2398.


Ketene→Dehydracetic acid→
(A)
Dihydroxyphenylacetic acid (ketonic form)
Diacetylacetone
−H₂O
Dimethylpyrone
+2H₂O
Methylation
(C)

In fact, methods have been pointed out for the possible syntheses of the carbohydrates themselves from ketene.[1]

The presence of a carbonyl group in lignin cannot be deduced from its reaction with sulphites. As is well known, sulphurous acid combines readily with an ethylene group; *e.g.*, citral reacts with sodium bisulphite to give the stable dihydrosulphonic derivative, $C_9H_{17}.(SO_3Na)_2.CHO$, that still retains the aldehyde group, since it reacts with phenylhydrazine.[2] Bucherer[3] found that some hydroxyl compounds combine readily with sulphurous acid. Resorcinol takes on three mols of H_2SO_3 to form an ester in which the SO_2 cannot be directly determined with iodine, but alkali splits it off readily.

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[1] J. N. Collie, *J. Chem. Soc.*, **91** (1907), 1812.

[2] F. Tiemann and F. W. Semmler, *Ber.*, **26** (1893), 2710; **31** (1898), 3314.

[3] H. Bucherer, *Z. angew. Chem.*, **17** (1904), 1068; *J. prakt. Chem.*, **69** (1904), 49; **70** (1904), 345; *Ber.*, **53** (1920), 1457–1459.

$$R.OH + NaHSO_3 = R.O.SO_2.Na + H_2O.$$

He is of the opinion that lignin behaves like the tannins, forming an ester-like compound and not a sulphonic acid. According to Fuchs and Elsner,[1] sulphites react with the tautomeric form of the phenols to give ketone-bisulphite compounds.

Phelps[2] found that "lignone" from sulphite liquor did not behave as a sulphonic acid derivative, since no phenols were obtained on fusion with alkali and there was no reaction with phosphorus pentachloride. He concluded that most of the sulphur is present as an acid sulphurous ether.

Lignin Isolated with Alkalis.—The lignin in lignocelluloses is rendered soluble by fusion with alkalis or by heating with alkaline solutions under pressure; in the cold the solubility is limited. Rasped wood extracted with water, 5 per cent hydrochloric acid, water, alcohol, ether, ammonia, and caustic soda (sp. gr. 1.10) was fused with potassium hydroxide at 185° by Lange.[3] Beech gave 12 per cent of lignin acids and 64 per cent of cellulose; oak, 14 per cent of lignin acids and 61 to 63 per cent cellulose; fir, 52 to 55 per cent cellulose. The alkaline filtrate from the cellulose gave on acidification lignin acids of the following composition:

	Beech, per cent	Oak, per cent
C	61.50; 61.28	60.78; 60.93
H	5.32; 5.44	5.45; 5.40

The lignin acids were partially soluble in alcohol. The soluble and insoluble acids were considered identical from the ultimate analyses and from the fact that the lignin acid insoluble in alcohol, became soluble in alcohol to a large extent after solution in caustic soda, and reprecipitation with sulphuric acid. The lignin acids did not show the usual color reactions for lignin.[4]

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[1] W. Fuchs and B. Elsner, *Ber.*, **52** (1919), 2281; **53** (1920), 886; **54** (1921), 245, 249; W. Fuchs and W. Stix, *Ber.*, **55** (1922), 658.

[2] E. B. Phelps, *U. S. Geol. Survey, Water-supply Paper*, **226** (1909), p. 28.

[3] G. Lange, *Z. physiol. Chem.*, **14** (1890), 15–30, 217–226.

[4] G. Lange, *l.c.*, p. 219.

	Beech, per cent	Oak, per cent	Fir, per cent
Soluble in alcohol:			
C	61.47	61.61	61.28
H	5.48	5.47	4.95
Insoluble in alcohol:			
C	59.04	58.83	60.51
H	5.37	5.15	5.22

Aside from cellulose and lignin acids there were formed, during the fusion, formic acid, acetic acid, traces of higher fatty acids, oxalic acid, protocatechuic acid, catechol, ammonia, and traces of higher bases.

Using Lange's method of fusion with caustic potash, Streeb[1] obtained from spruce wood a lignin acid containing 64.59 per cent C and 5.35 per cent H. Acidification of the spent liquor from the manufacture of soda cellulose yielded a brown powder of variable composition: 62.94 to 65.50 per cent C; 5.11 to 5.39 per cent H; and 5.78 to 5.98 per cent CH_3. The lignin acids corresponded to the formula $C_{36}H_{44}O_{14}$ or $C_{36}H_{40}O_{12}$ and closely resembled the lignin acids of Lange. The acids were readily soluble in ammonia and caustic alkalis, difficultly soluble in alkali carbonates, insoluble in water, chloroform, benzene, and ether, and partially soluble in ethyl acetate and alcohol.

Heuser[2] has stated that no oxalic acid was formed by the fusion of carbohydrate-free lignin with caustic potash at temperatures up to 270°. It was later[3] found that a 20 per cent yield of oxalic acid was obtainable when four parts of lignin were heated with 50 parts of caustic potash at 280° for 40 minutes. The alkaline fusion of ligninsulphonic acid gives vanillic or protocatechuic acid, catechol, acetic acid, and traces of higher fatty acids.[4]

According to Hönig and Fuchs,[5] the alkaline fusion of ligninsulphonic acids gives no phenolic body other than protocatechuic acid. The yield is 13 to 19 per cent, based on the organic portion. The sulphonic group of the barium salts employed was not completely removed until a temperature of 250 to 300°C. was reached. It is, accordingly, believed that ligninsulphonic acids contain the carbon skeleton of protocatechuic acid.

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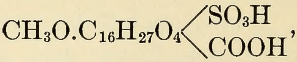
[1] E. Streeb, Diss. Göttingen (1892).

[2] E. Heuser, H. Roesch, and L. Gunkel, *Cellulosechemie*, **2** (1921), 113.

[3] E. Heuser and A. Winsvold, *Cellulosechemie*, **2** (1921), 113.

[4] K. H. A. Melander, *J. Soc. Chem. Ind.*, **38** (1919), 625A.

[5] M. Hönig and W. Fuchs, *Monatsh.*, **40** (1919), 341.

The three barium salts[1] obtained from sulphite liquor on boiling with a saturated aqueous solution of barium hydroxide are converted into different insoluble compounds and soluble substances.[2] They are apparently identical with one another in composition and agree with the formula $C_{18}H_{30}O_{10}SBa$. The latter is probably derived from an acid,  $CH_3O.C_{16}H_{27}O_4\left\langle\begin{matrix}SO_3H\\COOH\end{matrix}\right.$, and has all the properties of a tannic acid of the catechu group. The salt in aqueous solution is almost quantitatively precipitated by hydrochloric acid and formaldehyde; it precipitates with gelatin and quinine hydrochloride, while hide powder absorbs about 70 per cent of the free acid. Iron and copper chlorides and lead acetate give greenish-gray, green, and white precipitates, respectively.

Lignin on fusion with potassium hydroxide in the presence of air gave protocatechuic acid (16 to 19 per cent), catechol (1 to 3 per cent), oxalic acid, and lignin acids.[3] Below 240° the main product of the fusion is lignin acid. When the fusion was conducted in an atmosphere of hydrogen or nitrogen, the yield of oxalic acid decreased and that of catechol increased to 9 per cent. When iron was present in the melt, the yield of catechol (23 per cent) increased, though the presence of protocatechuic acid could no longer be detected. Protocatechuic acid appears to be an intermediate product in the formation of catechol. In these results is seen additional evidence for the belief that lignin contains a benzenoid nucleus.

Erdmann[4] on fusing purified fir wood with two parts of potassium hydroxide obtained acetic acid, catechol, and succinic acid. The source of the succinic acid (m.p. 180°) was attributed to the sugar-producing portion of the wood. Bente[1] also obtained succinic acid by the alkaline fusion of wood. Lange[2] was unable to confirm the findings of Erdmann with respect to the formation of succinic acid, though it has recently been identified in the alkaline fusion of "wood gum" from beech.[3] It has also been obtained by the oxidation of Willstätter's lignin with hydrogen peroxide.[4]

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[1] M. Hönig and J. Spitzer, *Monatsh.*, **39** (1918), 1.

[2] M. Hönig and J. Spitzer, *Monatsh.*, **41** (1920), 215–222.

[3] E. Heuser and A. Winsvold, *Ber.*, **56** (1923), 902–909; *Cellulosechemie*, **4** (1923), 49–58, 62–68.

[4] J. Erdmann, *Ann. Suppl.*, **5** (1867), 228. The erroneous reference (*Ann.*, **138** (1866), 1) cited by Lange has been repeatedly copied in the literature.

Beckmann[5] used various alkaline solutions for obtaining lignin from the straw of winter rye, and worked in the cold to avoid as much as possible a chemical change in the lignin. The best method consisted in treating the straw with a 2 per cent sodium hydroxide solution made from 600 cubic centimeters of 96 per cent alcohol, 20 grams of sodium hydroxide, and 400 cubic centimeters of water. The free alkali was neutralized with hydrochloric acid, the alcohol distilled off under reduced pressure, and the lignin precipitated with acid. Three extractions gave 7 per cent of lignin, while the residual straw retained 15 per cent of lignin as determined with fuming hydrochloric acid. The relationship of the easily to the difficultly soluble lignin remains to be determined.

The lignin was readily soluble in basic solvents, such as pyridine, and acid solvents, such as the phenols. Various preparations gave on analysis:

	Per Cent
C	61.80–63.01
H	5.45– 5.78
CH_3O	14.34–15.81
Ratio C:CH_3O, about	10:1

The results agree with the formula $C_{40}H_{44}O_{15}$ (mol. wt. 764.6). The sodium salt of the lignin contained somewhat less than two atoms of sodium. By the freezing-point method with phenol, the molecular weight varied from 762 to 1057, and by the boiling-point method with glacial acetic acid, from 768 to 891. Arylation established the presence of four hydroxyl groups, so that the formula may be represented by

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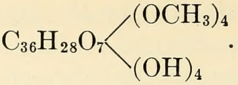
[1] F. Bente, *Ber.*, **8** (1875), 478.

[2] G. Lange, *Z. physiol. Chem.*, **14** (1890), 223.

[3] F. König, *Cellulosechemie*, **2** (1921), 118.

[4] E. Hägglund and C. B. Björkman, *Biochem. Z.*, **147** (1924), 74.

[5] E. Beckmann, O. Liesche, and F. Lehmann, *Z. angew. Chem.*, **34** (1921), 285–288; *Biochem. Z.*, **121** (1921), 293–310.



$$C_{36}H_{28}O_7\begin{cases}(OCH_3)_4\\(OH)_4\end{cases}.$$

The effect of 1.5 per cent caustic soda on the lignins of wood and straw has been studied at room temperature, at the boiling point, and at 3, 6, and 9 atmospheres' pressure.[1] For woods, pressures of 6 and 9 atmospheres were necessary to remove all the lignin. The methoxyl content of the lignin obtained at 6 atmospheres' pressure was, in general, at a maximum. The total lignin obtained was always less than by the Willstätter method. Maple (*Acer negundo*) and pine (*Pinus silvestris*) lignins on reduction with hydriodic acid gave complex substances of the formulæ $C_{72}H_{65}O_{12}I$ and $C_{108}H_{98}O_{18}I$, respectively.

All natural lignins, according to Powell and Whittaker,[2] are derived from lignol, a polyhydroxy compound of the formula $C_{38}H_{30}O_4.(CO)_2.(CHO).(OH)_9$. Lignins differ from each other in the number of methoxyl groups, which may be three to five. Data on the various lignins and their derivatives are given below:

Substance analyzed	Determination	Source of lignin						
		Flax, per cent	Larch, per cent	Pine, per cent	Spruce, per cent	Ash, per cent	Birch, per cent	Poplar, per cent
Lignin	C	63.9	63.8	63.4	64.0	63.2	63.2	63.3
	H	5.8	5.2	5.6	5.5	5.6	5.5	5.8
	−CHO	3.1	....	2.9	3.1	....	3.2	
Acetyl-lignin	−OCH_3	11.8	9.0	11.5	11.0	13.3	15.2	12.6
	−$CO.CH_3$	20.5	23.0	18.9	19.4	17.6	14.5	17.5
	Number of methyl groups	4.0	3.1	3.9	3.8	4.5	5.0	4.3
	Number of acetyl groups	5.0	5.8	4.5	4.8	4.3	3.4	4.3
	Total groups	9.0	8.9	8.4	8.6	8.8	8.4	8.6
Acetyl-methyl-lignin	−OCH_3	20.3	19.9	20.4	23.1	20.0	22.4	22.7
	−$CO.CH_3$	11.1	11.8	10.5	8.0	11.3	8.1	7.5
	Number of methyl groups	6.5	6.4	6.5	7.2	6.4	7.0	7.0
	Number of acetyl groups	2.6	2.7	2.4	1.8	2.6	1.8	1.7
	Total groups	9.1	9.1	8.9	9.0	9.0	8.8	8.7

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[1] E. Beckmann, O. Liesche, and F. Lehmann, *Biochem. Z.*, **139** (1923), 491–508.

[2] W. J. Powell and H. Whittaker, *J. Chem. Soc.*, **125** (1924), 357–364; **127** (1925), 132–137.

Examination of acetylated lignin showed that the total number of acetyl and methoxyl groups present represented nine hydroxyl groups, though the actual number may be eight to ten in lignin. The presence of an aldehydic group is shown by reduction of Fehling's solution; and since methyllignin reacts with three molecules of phenylhydrazine, two ketonic groups are probably present also. The insolubility of acetylated lignin in cold alkali indicates the absence of a carboxyl group. No information is given on the degree of acetylation of the lignin as it occurs in nature.

The lignin was isolated by heating the raw material with 8 to 12 per cent sodium hydroxide solution under pressure at 130 to 160°, precipitating it with hydrochloric acid, and purifying by reprecipitation. It is assumed that by these treatments the lignin undergoes only slight change. This requires confirmation. It has been observed (Chap. XII) that a mild preliminary treatment of coniferous woods with either alkalis or acids renders the lignin much more difficult to remove than from the raw wood on cooking by the sulphite process.

Lignin Isolated with Strong Mineral Acids.—The power of strong mineral acids to dissolve cellulose has long been known. Béchamp[1] employed strong sulphuric and hydrochloric acids, while in 1868 use was made of 72 per cent sulphuric acid for determining "ligneous cuticul."[2] Hydrochloric acid of a concentration of 40 to 42 per cent attacks wood rapidly. Spruce wood gave 30 per cent of lignin that was obtained purer than that by the use of sulphuric acid.[3] The lignin so isolated is much darker than the original lignocellulose, apparently as a result of dehydration. In this way was explained the darkening action of strong sulphuric acid on the light-yellow lignin obtained as a residue from elder pith by the action of cuprammonium solution.[4]

König[5] has described several forms of lignin: Protolignin is rendered soluble by enzymes or water under a steam pressure of 2 to 3 atmospheres; hemilignin is dissolved by heating with 1 to 3 per cent mineral acids at 1 to 3 atmospheres' pressure; ortholignin is partially dissolved by concentrated acids. The portion dissolving without coloration is colorless ortholignin, the residue, colored ortholignin. Unfortunately, most of the painstaking analytical work was done on "crude fiber," so that the results are difficult to correlate. The lignin obtained by the use of 72 per cent sulphuric acid contained a small amount of sulphuric acid that could not be removed by washing. Fir and beech lignin retained 0.045 per cent SO_3.[1] Wood, purified by extraction with water and alcohol-benzene, after treatment with 41 per cent hydrochloric by the Willstätter method, gave lignins with the following composition:[2]

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[1] A. Béchamp, *Ann. chim. phys.*, **48** (1856), 463; *Compt. rend.*, **42** (1856), 1213.

[2] E. Fremy and A. Terreil, *Bull. soc. chim.*, **9** (1868), 439.

[3] R. Willstätter and L. Zechmeister, *Ber.*, **46** (1913), 2401.

[4] E. Fremy and Urbain, *Compt. rend.*, **94** (1882), 109.

[5] J. König and E. Rump, "Chemie und Struktur der Pflanzen-Zellmembran" (1914), p. 85.

	Fir lignin from		Beech lignin from	
	Wood, per cent	Crude fiber, per cent	Wood, per cent	Crude fiber, per cent
Carbon	62.62	66.15	60.95	63.72
Hydrogen	5.24	4.09	6.20	4.42

Hägglund[3] prepared lignin from spruce, previously extracted with acetone and ether, by treating one part of wood with 10 parts of 43 per cent hydrochloric acid and allowing to stand 15 minutes. The yield was 28 per cent. The lignin gave the characteristic reactions with phloroglucinol, aniline sulphate, dimethyl-*p*-phenylenediamine, and ferricyanide, but not the Mäule reaction. The lignin contained 3.5 per cent hygroscopic moisture,1.63 per cent chlorine, 0.11 per cent nitrogen, and 0.95 per cent ash. Correcting for these constituents, elementary analysis showed: C, 65.47 per cent; H, 5.47 per cent. Since the wood contained 4.98 per cent CH_3O, the methoxyl content of the lignin should be 17.8 per cent; due to the action of the hydrochloric acid, however, the isolated lignin contained but 14.39 per cent CH_3O.

Since the lignin gave 3.69 per cent of furfural, it was apparently not free from pentosans. The lignin showed the following solubilities in various reagents:

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[1] J. König and E. Rump, *l.c.*, p. 57.

[2] J. König and E. Rump, *l.c.*, p. 67.

[3] E. Hägglund, *Arkiv Kemi, Mineral. Geol.*, **7,** 8 (1918), 1–20.

Reagent	Concentration, per cent	Temperature, degrees Centigrade	Time, hours	Solubility, per cent
Sodium bisulphite	5	140	5	12
Calcium bisulphite	4	140	5	Traces
Sodium hydroxide	10	100	2	15.2
Sodium hydroxide	5	170	3	97.8

The lignin prepared by Heuser,[1] by two treatments of spruce with 42 per cent hydrochloric acid, contained in the air-dry state 9.25 per cent moisture and 0.485 per cent ash. It had a copper number of 12.9, a methyoxyl content of 14.0 per cent, and gave no furfural on distillation with hydrochloric acid.

The lignin obtained by treating spruce with 45 per cent hydrochloric acid at 0° for 15 minutes contained 4 per cent of pentosan, identified as araban, so that Hägglund[2] considers the carbohydrate to be an integral part of the lignin. After removal of the pentosan from the lignin by hydrolysis, the copper number increased from 7.85 to 25.9. With 41 per cent hydrochloric acid, the lignin showed 6.64 per cent of pentosan after ½ hour and this decreased only slightly, to 6.38 per cent, after 12 hours.[3] Kürschner[4] likewise states that a lignin free from pentosan is obtained only after the prolonged action of cold fuming hydrochloric acid or hot dilute acid. After 3 hours' action, the lignin contained 6 per cent of pentosans. Since xylose was obtainable from the ligninsulphonic acids from sulphite liquor, and from the lignin acids from soda liquor, he also concludes that some xylan is combined with the lignin. On the other hand, Powell and Whittaker[5] found less than 1 per cent of pentosan in lignins isolated from wood with alkali, and this disappeared on purification.

The lignin isolated by Ungar[6] by the action of hydrochloric acid (sp. gr. 1.204) on spruce for 25 hours contained almost all the methoxyl of the wood (15.2 per cent), about 2.5 per cent of chlorine, and gave 2.02 per cent furfural.

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[1] E. Heuser and C. Skiöldebrand, *Z. angew. Chem.*, **32** (1919), 41.

[2] E. Hägglund and C. J. Malm, *Cellulosechemie*, **4** (1923), 73; *Ber.*, **56** (1923), 1866.

[3] E. Hägglund, *Cellulosechemie*, **4** (1923), 84.

[4] K. Kürschner, *Naturprodukte*, **24** (1923), 36.

[5] W. J. Powell and H. Whittaker, *J. Chem. Soc.*, **127** (1925), 132.

[6] E. Ungar, "Beiträge zur Kenntnis der Verholzten Faser," Diss. Budapest (1916), p. 63.

Klason,[1] using 64 per cent sulphuric acid, obtained from spruce a lignin with C, 63.97 per cent; H, 5.32 per cent; and retaining 1.70 per cent pentosan.

Heuser[2] denies that pentosans are chemically combined with the lignin, their presence being due to incomplete hydrolysis. Xylan is more resistant to hydrolysis by fuming hydrochloric acid than by the hot dilute acid.

Pine wood after exhaustion with acetone and ether contained 22 to 26 per cent of lignin by Willstätter's method. By alternate treatment with cold concentrated hydrochloric acid and boiling dilute acid, more than half of the lignin was dissolved. The dissolved portion contained arabinose, and a fermentable sugar, but no methylpentose. Since lignin free from carbohydrates is colored brown and gives a violet solution with strong hydrochloric acid, while wood and its solution are colored green under the same treatment, it is concluded that a union exists between lignin and carbohydrates in the wood.[3]

This opinion is supported by the work of Miller and Swanson,[4] who find that when wood is cooked by the sulphite process, the lignin behaves as if it were chemically combined with the easily hydrolyzable carbohydrates. Klason[5] has suggested that lignin is combined with the hemicelluloses by an acetal linkage.

Lignin, like humin substances, in the opinion of Jonas,[6] is a condensed furan body and does not have a benzenoid structure. The dark-brown amorphous lignins isolated from the various conifers by the Willstätter method are identical in properties and composition. This lignin differs from the uncolored lignin in the plant, in that it is more highly polymerized, no longer contains acetyl groups, and is the methyl ester of a ketocarbonic acid. Its dark color is perhaps due to a carbonyl group, not originally present in the lignin, that could be formed by rearrangement of the primary hydroxyl group resulting from the splitting off of an acetyl group. In Willstätter lignin, methyl groups occur in combination both as esters and ethers. When treated with hydrogen bromide in glacial acetic acid, the lignin is completely demethylated, becoming deep black and insoluble in all solvents. During demethylation, by rearrangement and splitting off of a carbonyl group, another furan ring is formed. This is supported by the fact that, in distinction from the original product, the lignin will not pass over to an acid on heating with caustic soda under pressure; also it will no longer dissolve in boiling phenol. The furan structure of lignin is also supported by Marcusson.[1]

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[1] P. Klason, *Cellulosechemie,* **4** (1923), 81; *Svensk Pappers.-Tid.,* **26** (1923), 319.

[2] E. Heuser, *Cellulosechemie,* **4** (1923), 77–78, 85.

[3] E. Hägglund and C. B. Björkman, *Biochem. Z.,* **147** (1924), 74–78.

[4] R. N. Miller and W. H. Swanson, "Chemistry of the Sulphite Process. VIII. Studies of the Acid Hydrolysis of Wood," Paper read at 69th Meeting *Am. Chem. Soc.* (1925).

[5] P. Klason, *Ber.,* **55** (1922), 455.

[6] K. G. Jonas, *Z. angew. Chem.,* **34** (1921), 289, 373.

Willstätter[2] reduced the lignin from pine and beech with hydriodic acid (sp. gr. 1.7) and red phosphorus under pressure at 250°, obtaining a product separable into an acid portion and a mixture of solid and liquid hydrocarbons. The latter mixture contained 88.14 per cent C and 11.85 per cent H. The molecular weight varied from 167 for the lowest liquid fraction to 842 for the highest solid. No definite compounds were isolated. *n*-Hexyl iodide is not an intermediate product. Similar hydrocarbons were obtained by the reduction of cellulose, glucose, and other carbohydrates, indicating that there is a close structural relationship between lignin and the carbohydrates. During reduction the hydrocarbons are probably first converted to furan derivatives, while in lignin the furan structure preexists. The hydrocarbons appear to be a mixture of polycyclic, hydrogenated, five- and six-membered ring compounds in which the number of rings becomes greater with increasing molecular weight. In the light of the results of Willstätter, Schrauth[3] assumes that since carbohydrates give hydroxymethylfurfural with strong acids, lignin may be formed by the condensation of three molecules of

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[1] J. Marcusson, *Z. angew. Chem.*, **34** (1921), 437; **35** (1922), 165; **36** (1923), 42.

[2] R. Willstätter, L. Kalb, and G. von Miller, *Ber.*, **55** (1922), 2637–2652.

[3] W. Schrauth, *Z. angew. Chem.*, **36** (1923), 149, 571; *Brennstoff-Chem.*, **4** (1923), 161; W. Schrauth and K. Quasebarth, *Ber.*, **57** (1924), 854.

5-oxymethylfurfural to give a benzophenanthrene derivative, $C_{18}H_{18}O_9$, which by reduction in the plant goes over to $C_{18}H_{18}O_6$. The derivative contains three—CO.CH_2—groups which render the compound very reactive. Enolization produces a double bond and a phenolic hydroxyl group capable of methylation or esterification.

Wood heated with formic or acetic acid containing 0.5 to 0.7 per cent of sulphuric acid gives a ligneous product insoluble in water, soluble in formic and acetic acids, and partially soluble in alcohol, petroleum ether, and benzene.[1]

Grüss[2] obtained a lignin alcohol, $C_{26}H_{46}O_{10}$, by boiling beech wood with alcoholic hydrochloric acid. The alcohol is precipitated with water as a yellowish powder, m.p. 160°. It gives characteristic colorations with the various phenolic lignin reagents, but does not show the Schiff reaction for aldehydes. The alcohol is soluble in alkalis and reprecipitable with acetic acid; if the precipitate is boiled with 1.5 per cent sulphuric acid it is no longer soluble in alkali. The alcohol on oxidation with hydrogen peroxide at 60 to 70° gives a lignin acid whose copper salt, $C_7H_{14}O_5Cu.5H_2O$, obtainable in α- and β-modifications, has the noteworthy property of being crystalline. Analysis showed:

	Per Cent
C	24.82
H	7.20
O	48.40
Cu	19.10

Wood dissolves readily in acetyl bromide, but slowly and incompletely in acetyl chloride. No action takes place unless moisture is present, so that the reaction is evidently one of hydrolysis and esterification. Zechmeister[3] found that when 2 grams of finely divided wood were treated with 20 grams of acetyl bromide, only traces remained undissolved after standing one day. After standing 2.5 days, ice precipitates a compound, m.p. 60 to 70°, soluble in alcohol, ether, and benzene, and containing 25.5 to 26.1 per cent bromine.

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[1] *Akt.-Ges. für Zellstoff-u. Papierfabr.*, G. P. 309551 (1916).

[2] J. Grüss, *Ber. botan. Ges.*, **41** (1923), 48–52, 53–58.

[3] L. Zechmeister, Diss. Zürich (1913), p. 46; *Ber.*, **56** (1923), 578.

Formulæ for Lignin

Year	Formula	Groups					Source	Method of isolation	Author	References
		CH_3O	$CH_3.CO$	OH*	CHO	CO				
1857	$C_{38}H_{24}O_{20}$	. .	. .	. .	.	. .	Wood	Indirect analysis	Schulze	*Chem. Centr.*, **28,** 321.
1882	$C_{19}H_{18}O_8$	. .	. .	. .	. .	. .	Wood	Indirect analysis	Schuppe	Diss. Dorpat.
1889	$C_{19}H_{21}O_9$	. .	. .	. .	. .	. .	Jute	Chlorine	Cross and Bevan	*J. Chem. Soc.*, **55,** 207.
1892	$C_{26}H_{30}O_{12}$	2	. .	2	. .	. .	Conifers	Sulphite liquor	Lindsey and Tollens	*Ann.*, **267,** 341.
1892	$C_{36}H_{44}O_{15}$	. .	. .	. .	.	. .	Spruce	Potassium hydroxide	Streeb	Diss. Göttingen.
1910	$C_{40}H_{42}O_{11}$	4	. .	7		. .	Spruce	Sulphite liquor	Klason	"Zusam. des Fichtenholzes."
1912	$C_{20}H_{22}O_{10}$	2	. .	2	1	4	Jute	Degradation	Cross and Bevan	"Researches," III, p. 104.
1917	$C_{69}H_{68}O_{20}$	6	. .	6	. .	. .	Conifers	Sulphite liquor	Klason	*Arkiv Kemi Mineral. Geol.*, **6,** No. 15, **1.**
1918	$C_{24}H_{25}O_9$	2	. .	2	. .	. .	....	Composite formula	Von Fellenberg	*Biochem. Z.*, **85,** 80.
1920	$C_{22}H_{22}O_7$ (α)	2	1	3	1	1	Spruce	Sulphite liquor	Klason	*Ber.*, **53,** 1864.
	$C_{19}H_{18}O_9$ (β)	. .	. .	. .	. .	. .	Spruce	Sulphite liquor	Klason	*Ber.*, **53,** 1864.
1921	$C_{40}H_{44}O_{15}$	4	. .	8	. .	. .	Rye	Alcoholic NaOH	Beckmann, *et al.*	*Biochem. Z.*, **121,** 293.
1922	$C_{22}H_{22}O_7$ (α)	3	1	5	1	. .	Spruce	Sulphite liquor	Klason	*Ber.*, **55,** 448.
1923	$C_{20}H_{20}O_6$ (α)	2	. .	4	1	. .	Spruce	Sulphite liquor	Klason	*Ber.*, **56,** 300.
	$C_{19}H_{18}O_7$ (β)	. .	. .	. .	. .	. .	Spruce	Sulphite liquor	Klason	*Ber.*, **56,** 300.
1924	$C_{26}H_{30}O_9$	2	. .	6	1	. .	Spruce	Sulphurous acid	Dorée and Hall	*J. Soc. Chem. Ind.*, **43,** 257T.
1924	$C_{45}H_{48}O_{16}$	4	. .	9	1	. .	Flax	Sodium hydroxide	Powell and Whittaker	*J. Chem. Soc.*, **125,** 357.
1925	....	3–5	. .	8–10	1	2	Wood	Sodium hydroxide	Powell and Whittaker	*J. Chem. Soc.*, **127,** 132.

* Total hydroxyl groups.

Five grams of dry beech or fir wood are immersed in 30 grams of acetyl bromide and let stand for 12 hours, whereby complete solution takes place. The amorphous granular precipitate, obtained by pouring on ice, is filtered off, washed with water, and then digested with alcohol to remove the cellulose derivative. The residual lignin derivative is obtained as a white amorphous powder by solution in acetone and precipitation with alcohol.[1]

Spruce lignin isolated by means of strong hydrochloric acid dissolves with much less rapidity than the wood, several months being required to render the greater portion soluble.[2]

Condensation Products of Lignin.—Phenols have the power to dissolve lignin at a temperature of about 200°.[3] By the addition of mineral acid to the phenol, the removal of the lignin is attained at a much lower temperature;[4] with 0.1 per cent sulphuric acid at 100° and with 1.0 per cent at 80°, the lignin can be removed in 4 to 5 hours.[5]

Hochfelder[6] heated spruce, dried at 100°, with phenol at 180° for 48 hours. The dissolved lignin was obtained in two forms. Distilling off the phenol and extracting the residue with ether left "lignin substance α" as a brown, amorphous powder, while "lignin substance β" was recovered from the ether as a resinous, syrupy mass. "Lignin substance α" has the formula $C_{22}H_{26}O_6$. It is insoluble in water, ammonia, soda, acetic acid, and benzene, and easily soluble in acetone, pyridine, and dilute caustic alkali. Carboxyl and carbonyl groups were absent, but the presence of three phenolic hydroxyl groups was shown by acetylation. Among the products resulting from the fusion of "lignin substance α" with potassium hydroxide were identified acetic acid, traces of formic and isobutyric acids, salicylic acid, *p*-oxybenzoic acid, protocatechuic acid, oxalic acid (7.8 per cent), lignin acids (13.64 per cent), pyrogallol (?), catechol, and phenol (6.19 per cent). Owing to the condensation of phenol with lignin, phenol, salicylic acid, and some of the other products listed cannot be assumed, with Hochfelder, as originating from the lignin itself. The α- and β-lignin substances contained, respectively, 1.83 and 0.59 per cent of pentosans.

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[1] P. Karrer and F. Widmer, *Helvetica Chim. Acta.*, **4** (1921), 700; **6** (1923), 817.

[2] E. Ungar, Diss. Budapest (1916), p. 77.

[3] F. A. Bühler, *Papier-Ztg.*, **25** (1900), 3526; *Chem. Ind.* (1903), 138.

[4] R. Hartmuth, G. P. 326705; 328783 (1919).

[5] E. Legeler, Diss. Berlin (1921); *Cellulosechemie*, **4** (1923), 61; L. Kalb and V. Schoeller, *Cellulosechemie*, **4** (1923), 37.

[6] L. Hochfelder, "Beiträge zur Kenntnis der Ligninsubstanzen," Diss. München (1915), 46 pp.

The solvent power of phenol is due to a condensation between the phenol and the lignin.[1] On treating Willstätter's lignin with boiling phenol, a condensation product is obtained that distills without decomposition between 230 to 240° at 10-millimeters pressure. This is "phenol-lignin *b*," a salve-like body. If the lignin is converted into an acid by heating with alkali under pressure before being condensed with phenol, there results "phenol-lignin *a*," a brown, amorphous, non-distillable product. Wood and Willstätter's lignin give identical phenol-lignins *a* and *b*. Phenol-lignin *a* has a certain resemblance to the phthaleins; with alkalis it gives a dark-colored acid, that by reduction gives an almost colorless dihydroacid. The latter on oxidation passes at once into dark-colored "phenol-lignin *a*-acid."

Bühler[2] proposed to use phenol for preparing pulp from wood, but obviously the method is impracticable, due to the loss of phenol. According to Legeler,[3] in preparing 45 kilograms of pure cellulose from 100 kilograms of dry wood, 36 kilograms of phenol remain condensed with the non-cellulose constituents. Carbohydrates, including cellulose, under certain conditions give, with phenol and a mineral acid, bodies similar to phenol-lignin.

The lignin residue obtained by the hydrolysis of wood, when condensed with phenol, gives a product having the character of a phenol.[4] It is difficultly soluble in alcohol and ether, but soluble in pyridine, phenol, acetone, and caustic soda. A similar product is obtained by heating wood with phenol and a small amount of hydrochloric acid at 90° for 1 hour.

Norway spruce took up 1.33 to 2.32 per cent of aniline corresponding to 0.41 to 0.73 per cent of —CHO groups; and 0.64

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[1] K. G. Jonas, *Z. angew. Chem.*, **34** (1921), 289.

[2] F. A. Bühler, *l.c.*

[3] E. Legeler, *Cellulosechemie*, **4** (1923), 61.

[4] L. Kalb and V. Schoeller, G. P. 365287 (1920).

per cent hydroxylamine corresponding to 0.56 per cent—CHO. According to experimental conditions, the wood condensed with 3.03 to 12.59 per cent of phloroglucinol dimethylether.[1]

Phloroglucinol combines with the lignocelluloses in a definite ratio under specified conditions.[2] The reaction depends upon the amount of phloroglucinol and the concentration of the acid used. In the case of coniferous ground wood, using an amount of 0.5 per cent phloroglucinol solution (in hydrochloric acid of sp. gr. 1.06) equal to 10 per cent of phloroglucinol based on the wood, 6.7 per cent is absorbed; with 1 per cent of phloroglucinol, the absorption is complete. If the wood after treatment with 10 per cent of phloroglucinol solution is allowed to air dry, 8.9 per cent of phloroglucinol, $C_6H_6O_3.2H_2O$, is combined due to a concentration within the wood of both phloroglucinol and hydrochloric acid.[3] Under the latter conditions, lignocellulose combines with 7.6 per cent pyrogallol. In the case of jute, acetylation or chlorination did not alter the reaction with phloroglucinol. The same is true if the jute has first been digested in the cold for 6 days with 33 per cent hydrochloric acid with a loss in weight of 17 per cent, consisting mainly of the constituents yielding furfural. The phenols evidently condense with the lignin, since they are not removed by ordinary hydrolytic reagents, and no longer give the characteristic reactions with iron salts.

The combination of a small amount of phloroglucinol with the lignocellulose produces a marked increase in the residue insoluble in 42 per cent hydrochloric acid.[4] Beech containing 30.1 per cent lignin, after combination with 5.1 per cent phloroglucinol, gave a "lignin" residue of 76.3 per cent. This striking change is attributed to a new cleavage in the lignocellulose.

Aromatic bases, such as dimethyl-*p*-phenylenediamine, phenylhydrazine, and hydroxylamine, react with lignocellulose, the amount of nitrogen fixed being roughly proportional to the quantity of the base employed. While adsorption appears to be a large factor, a small portion of the base is evidently definitely combined with aldehydic groups in the lignocellulose.[1]

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[1] E. Ungar, Diss. Budapest (1916), p. 38.

[2] C. F. Cross, E. J. Bevan, and J. F. Briggs, *Ber.*, **40** (1907), 3119–3126.

[3] C. F. Cross and E. J. Bevan, *J. Soc. Dyers Colourists*, **32** (1916), 135.

[4] C. F. Cross and C. Dorée, "Researches," **4** (1922), p. 169.

Lignin, obtained from straw by alkaline digestion, on heating with phenylhydrazine gave an amorphous phenylhydrazone, $C_{58}H_{57}N_6O_{10}$, soluble in alcohol, acetone, and tetrachlorethane; with the atter solvent, transparent varnish-like coatings are obtainable.[2] When 1.5 parts of lignin were heated for 2 hours with one part of nitrosodimethylaniline, one part of concentrated hydrochloric acid, and 50 parts of alcohol, there was obtained lignocyanine, $C_{101}H_{103}N_{16}O_{26}$, resembling gallocyanine. It dyes silk and mordanted cotton a brownish violet. The heating of equal parts of lignin, aniline, and oxalic acid at 180° for 30 minutes gave a condensation product containing 4.7 per cent nitrogen. This corresponds with a compound, $C_{58}H_{60}N_3O_{10}$, containing three molecules of aniline to one of lignin.[3] A brown sulphur dye, $C_{36}H_{49}S_6O_{21}$, is obtained on fusion with sodium sulphide. In its various reactions straw cellulose acts as a trivalent substance, hence containing three aldehydic or ketonic groups. Further support for its aldehydic nature is found in the fact that an alkaline solution of straw lignin used on hides results in a soft-brown leather, without increase in weight, while a skin treated with an alkaline solution of sulphite liquor increased in weight about 75 per cent but was not tanned, and became hard and brittle after drying. None of the condensation products are definite substances, and their formation throws little light on the structure of lignin.

Action of Halogens.—Payen,[4] in 1839, observed that chlorine had both a bleaching and a yellowing action on wood. Von Baumhauer[5] also used chlorine gas in investigating the composition of fruit pits. A quantitative method for the determination of cellulose was developed by Fremy and Terreil[6] through the observation that after treatment with chlorine the incrusting materials became soluble in alkalis. Bevan and Cross[1] boiled the chlorinated fibers in sodium sulphite solution, a modification largely retained today. Sodium bisulphite is much less efficient than sodium sulphite for dissolving the chlorinated lignin, showing that an alkaline reagent is required.[2]

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[1] C. F. Cross, E. J. Bevan, and J. F. Briggs, *Ber.*, **40** (1907), 3119; C. F. Cross and E. J. Bevan, *J. Soc. Dyers Colourists*, **32** (1916), 135.

[2] F. Paschke, *Cellulosechemie*, **3** (1922), 19–21.

[3] F. Paschke, *Cellulosechemie*, **4** (1923), 31–32.

[4] A. Payen, *Compt. rend.*, **9** (1839), 149.

[5] E. H. von Baumhauer, *J. prakt. Chem.*, **32** (1844), 212.

[6] E. Fremy and A. Terreil, *Bull. soc. chim.*, **9** (1868), 439.

Cross and Bevan[3] by the direct chlorination of jute obtained a lignin chloride, $C_{19}H_{18}O_9Cl_4$, with 26.8 per cent chlorine. While dissolving most readily in alkaline solutions, lignin chloride also dissolves in glacial acetic acid and alcohol. In the case of jute, the weight of chlorine reacting is 16 to 17 per cent of the weight of the fiber, 8.0 to 8.5 per cent appearing as hydrochloric acid; hence, the reaction is one of simple substitution. Dry lignocellulose does not react with chlorine even when heated with it at 60 to 80°. In the case of woods, the amount of hydrochloric acid formed is considerably greater. The following results are based on wood previously exhausted with 1 per cent caustic soda.[4]

	Pine, per cent	Beech, per cent	Sycamore, per cent	Birch, per cent
Combined chlorine........	7.5	7.5	9.0	7.0
Acidity (as HCl)..........	23.5	19.5	21.0	15.0

One gram of jute[5] absorbed 60 cubic centimeters of chlorine at 18°.

The furfural-producing carbohydrates are not changed by chlorination, since the yield of furfural from a fiber is the same before and after chlorination.[6] Hägglund[7] obtained furfural from spruce lignin isolated with strong hydrochloric acid, but after chlorination of the lignin no furfural was obtainable. The chlorine content of the lignin was not uniform, varying from 39.7 to 46.2 per cent.

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[1] E. J. Bevan and C. F. Cross, *Chem. News*, **42** (1880), 80.

[2] A. W. Schorger, *J. Ind. Eng. Chem.*, **9** (1917), 561.

[3] "Cellulose" (1895), p. 102; *cf. J. Chem. Soc.*, **55** (1889), 199.

[4] C. F. Cross and E. J. Bevan, "Cellulose" (1895), p. 195.

[5] E. J. Bevan and C. F. Cross, *Chem. News*, **58** (1888), 215.

[6] "Cellulose" (1916), p. 136.

[7] E. Hägglund, *Arkiv Kemi, Mineral. Geol.*, **7** (1918), 18.

Heuser and Sieber,[1] in studying the action of chlorine on spruce wood, found (Fig. 3) that up to the point (2 hours) where all the lignin was removed, 31.1 per cent of chlorine was obtained as hydrochloric acid, while only 9.47 per cent had combined with the lignin; accordingly, the action of chlorine on wood lignin at least is mainly one of oxidation. Chlorination when extended to 22 hours resulted in a residue of oxycellulose, though the loss in weight was comparatively slight. As long as lignin remained there was practically no formation of oxycellulose. The lignin chloride gave on analysis: C = 47.03 per cent; H = 4.59 per cent; Cl = 22.68 per cent. Lignin chloride is not considered to be a uniform compound nor to have a cyclic structure, since it could not be reduced to a derivative of pyrogallol, as claimed by Cross and Bevan. It did not give a trace of furfural on distillation with 12 per cent hydrochloric acid. Fusion with caustic alkali gave large amounts of oxalic acid.

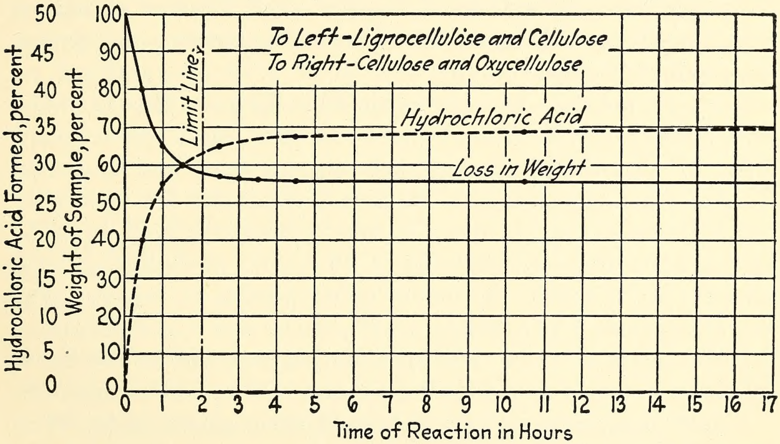

FIG. 3.—Progressive action of chlorine on spruce wood. (*After Heuser and Sieber.*)

Jonas[2] claims that if Willstätter's lignin is carefully chlorinated with good cooling, one and the same chloride is always obtained. Chlorination is accompanied by a partial oxidation, the light-yellow lignin chloride obtained being soluble in alkali, alcohol, and acetone.

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[1] E. HEUSER and R. SIEBER, *Z. angew. Chem.*, **26** (1913), 801–806.

[2] K. G. JONAS, *Z. angew. Chem.*, **34** (1921), 289.

Straw lignin, at room temperature, gave with sulphuryl chloride a pale-brown amorphous compound, $C_{37}H_{42}S_3Cl_3O_{12}$, free from methoxyl groups.[1] When the reaction was performed by heating in a sealed tube for 1 hour at 100°, there was obtained a yellow resinous body, $C_{36}H_{42}Cl_{11}O_{10}$, free from sulphur but containing 38.22 per cent chlorine. A lignin derivative, $C_{38}H_{46}Cl_5O_{15}$, containing only 19.18 per cent chlorine, resulted from the action of two parts of phosphorous pentachloride in tetrachlorethane.

Lignin is profoundly chlorinated when boiled for 3 hours with antimony pentachloride containing a small amount of iodine. Perchlorethane and, apparently, hexachlorobenzene are among the products formed.[2]

Bromine behaves towards lignin like chlorine, though much less energetically. Müller[3] removed the lignin from plant fibers by alternate treatment with bromine water and ammonia. A greater combination with bromine is obtained if the lignocellulose is first dissolved in zinc chloride-hydrochloric acid, bromine added, and, after standing about 16 hours, precipitating with water.[4] In this way the non-cellulose portion of esparto gave the compounds $C_{17}H_{14}Br_4O_6$, $C_{15}H_{12}Br_4O_5$, and $C_{27}H_{28}Br_4O_{10}$.

Iodine appears to be without chemical reaction on the lignocelluloses, forming as with cellulose[4] only adsorption compounds.

Lignin isolated from flax and wood with caustic soda, when suspended in carbon tetrachloride and treated with chlorine, gives a brick-red solid having the formula $C_{40}H_{20}O_8Cl_{12}(OCH_3)_2.(OH)_5.CHO$. Regenerated with acids from its solution in cold alkali, it has only 6 chlorine atoms. The bromolignin is a dark-red solid similar to chlorolignin.[5]

Acetyl and Formyl Groups.—The ease with which acetic and formic acids may be obtained by the use of hydrolytic agents indicates that acetyl and formyl groups are present in the lignocelluloses as a part of the lignin. Cross and Bevan[1] obtained 7 to 8 per cent of acetic acid by treating beech wood with dilute alkalis. Acetic acid is also obtainable by digesting woods with dilute sulphuric acid at 60 to 100°. Larger yields are obtainable by treating the wood with cold concentrated sulphuric acid, diluting, and distilling.

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[1] F. Paschke, *Cellulosechemie*, **3** (1922), 19.

[2] H. Tropsch, *Ges. Abhandl. Kenntnis. Kohle*, **6** (1921), 301–302.

[3] Hugo Müller, "Die Pflanzenfaser." In A. W. Hoffmann's "Bericht über die Entwichlung d. Chem. Industrie," **2** (1877), 27.

[4] C. F. Cross and E. J. Bevan, "Cellulose" (1916), p. 138.

[5] W. J. Powell and H. Whittaker, *J. Chem. Soc.*, **125** (1924), 357; **127** (1925), 132.

Cross[2] and his associates found that on distilling celluloses with sulphuric acid the amount of volatile acids, particularly formic, increased greatly with the strength of the sulphuric acid. Barley straw gave 1.7 and 14.8 per cent of volatile acids, calculated as acetic acid, with 10 and 50 per cent sulphuric acid, respectively. The amounts of acid given by various celluloses on distilling with 40 to 50 per cent sulphuric acid were:

	Acetic acid, per cent	Formic acid, per cent
Swedish filter paper	2.7	17.2
Esparto cellulose	3.2	16.6
Bleached cotton	3.1	13.2
Raw cotton	5.0	9.4
Jute cellulose	4.9	22.7
Beech-wood cellulose	3.5	14.6

If the presence of acetyl groups is a characteristic feature of lignification, there must be a marked difference between the lignins of hardwoods and conifers. On boiling with 2.5 per cent sulphuric acid for 3 hours the hardwoods give 4.30 to 5.79 per cent acetic acid and the conifers 0.71 to 1.79 per cent.[3] A slight amount of formic acid is formed simultaneously, but it is questionable if formyl groups are actually present, since it is characteristic of hexose carbohydrates to decompose to lævulinic and formic acids on boiling with dilute acids.

Data have been obtained by Dore[4] indicating that acetyl groups may sometimes be associated with the cellulose. Due to saponification by the strong acid, only a small amount of acetic acid remains in the lignin. As would be expected, the acetyl groups are completely removed by digestion in the cold with 5 per cent sodium hydroxide.[1] The acetic acid should exist in the solution as sodium acetate and not as "substances yielding acetic acid on hydrolysis."

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[1] "Cellulose" (1895), p. 191.

[2] C. F. Cross *et al.*, *Ber.*, **28** (1895), 1940.

[3] A. W. Schorger, *J. Ind. Eng. Chem.*, **9** (1917), 556.

[4] W. H. Dore, *J. Ind. Eng. Chem.*, **12** (1920), 475.

DISTRIBUTION OF ACETIC ACID IN REDWOOD

	ACETIC ACID, PER CENT
Original wood	0.83
Cellulose (by chlorination)	0.55
Lignin (by 72 per cent H_2SO_4)	0.09

Cross and Bevan[2] are of the opinion that the acetic acid is derived from ketene derivatives rather than from acetyl groups.

The formation of acetic and formic acids by the acid hydrolysis of lignocelluloses is definitely attributed to the presence of acetyl and formyl groups.[3] Beech wood, on treatment in an autoclave for 3 hours with 1 per cent sulphuric acid, gave 5.2 per cent of acid, as acetic acid. Formic acid was present, but higher fatty acids and lævulinic acid were not detected. Spruce ground wood gave 1.06 per cent of acetic acid and 0.21 per cent of formic acid, the ratio being 1:5. Spruce wood that had been hydrolyzed twice with acid under pressure gave, after washing and drying, 2.27 per cent of acid on destructive distillation. The original wood gave only a slightly greater yield of acid, namely, 2.43 per cent, on destructive distillation.

Guijo, a Philippine wood having a marked corrosive action on metal fastenings, yielded 0.2 per cent of acetic and formic acids on leaching with cold water.[4] This acidity may be due to a gum such as that produced by *Cochlospermum gossypium*, a small deciduous tree growing in India, which has the property of giving off acetic acid on exposure to moist air. It yields 14.4 per cent of acetic acid on hydrolysis with sulphuric acid.[5] Cross and Tollens[1] found that "wood gum" gave no acetic acid on hydrolysis.

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[1] W. H. DORE, *J. Ind. Eng. Chem.*, **12** (1920), 986.

[2] C. F. CROSS and E. J. BEVAN, "Researches" (1905–1910), p. 103; (1910–1921), p. 164.

[3] W. E. CROSS and B. TOLLENS, *J. Landw.*, **59** (1911), 185–196; *Ber.*, **43** (1910), 1526–1528.

[4] A. W. SCHORGER, *J. Ind. Eng. Chem.*, **9** (1917), 561.

[5] H. H. ROBINSON, *J. Chem. Soc.*, **89** (1906), 1496.

The acetyl content of wood was determined by Pringsheim and Magnus[2] by heating it with eight times its weight of 3.5 per cent sodium hydroxide solution at 6 atmospheres for 6 hours. Pine wood gave 4.2 per cent acetic acid. Repetition of the treatment for 3 hours gave an additional 1.5 per cent, while a third treatment gave only a trace. In comparison with 5.7 per cent of acetic acid from pine, hornbeam gave 10.5 per cent of acetic acid. The acetyl groups of Willstätter's lignin are completely removed by the acid treatment, but can be restored by acetylation, the product becoming appreciably lighter in color by the operation. The lignin of coniferous wood contained 19.85 per cent acetic acid and the lignin of hornbeam 37.8 per cent, as determined by acetylation and subsequent saponification. On the basis of 23 per cent lignin (Willstätter) and 10.5 per cent acetic acid by the alkaline hydrolysis of hornbeam, and 30 per cent lignin and 5.7 per cent of acetic acid from pine, the acetic acid content of the acetylated lignin is 5 to 7 per cent higher than in the original lignin. It is claimed by the authors that the acetyl groups of wood cannot be completely saponified by heating for 3 hours with 2.5 per cent sulphuric acid and that the increased yield of acetic acid by alkaline saponification is due in only small part to the cellulose. This is scarcely correct. Their data show that a wood cellulose freed from lignin by the chlorination method, and from pentosans by glycerol-sulphuric acid mixture, gave 3.05 per cent acetic acid when boiled with caustic soda, and 4.6 per cent acetic acid with alkali at 4 atmospheres pressure. It has been quite correctly objected that probably only about one-third of the acetic acid obtained by the Pringsheim method has its source in the lignin.[3]

When finely divided wood is extracted with an alkaline solution at ordinary temperature or by gentle heat at atmospheric pressure, fatty acids are obtained, consisting mainly of acetic acid, with 1 to 3 per cent of formic acid and a trace of butyric acid. Pine wood gives 1 to 2 per cent of acids, and beech 5 to 6 per cent.[1]

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[1] *L.c.*

[2] H. Pringsheim and H. Magnus, *Z. physiol. Chem.*, **105** (1919), 179–186; *Z. angew. Chem.*, **33** (1920), 56.

[3] C. Schwalbe and E. Becker, *Z. angew. Chem.*, **33** (1920), 225.

Methoxyl Groups.—The methyl groups in wood occur largely as ethers, but a small part apparently as an ester. In an extensive investigation of the methyl content of wood Benedict and Bamberger,[2] using the Zeisel method, showed that the presence of CH_3O groups was characteristic of lignification. Cotton and filter paper gave no methoxyl and sulphite cellulose but 0.70 per cent. In the following table the original methyl numbers have been recalculated to methoxyl.

Species		CH_3O, per cent
Maple (*Acer pseudoplatanus L.*)	Trunk	6.30
Locust (*Robinia pseudacacia L.*)	Branch	4.88
Birch (*Betula alba* L.)	Trunk (3 years old)	5.29
Pear (*Pyrus communis* L.)	Trunk	6.61
Oak (*Quercus pedunculata* Ehrh.)	Trunk	5.42–5.87
Alder (*Alnus glutinosa* Gart.)	Trunk	5.95
Ash (*Fraxinus excelsior* L.)	Trunk	5.58
Ash (*Fraxinus excelsior* L.)	Branch	6.22
Spruce (*Abies excelsa* D. C.)	Trunk	4.43–4.92
Spruce (*Abies excelsa* D. C.)	Trunk (center)	5.33
Spruce (*Abies excelsa* D. C.)	Trunk (periphery)	4.78
Pine (*Pinus sylvestris* L.)	Trunk	4.63
Larch (*Larix europea,* D. C.)	Trunk	4.10–5.52
Fir (*Abies pectinata* D. C.)	Trunk	5.05
Linden (*Tilia parvifolia* Ehrh.)	Trunk	5.27
Mahogany (*Swietenia mahogoni* L.)	Trunk	5.48
Walnut (*Juglans regia* L.)	Trunk	4.68–5.54
Poplar (*Populus alba* L.)	Trunk	5.33
Beech (*Fagus silvatica* L.)	Trunk	5.40–6.22
Elm (*Ulmus campestris* L.)	Trunk	6.01
Willow (*Salix alba* L.)	Trunk	4.76
Hornbeam (*Carpinus betulus* L.)	Trunk	5.48

The authors conclude that, in general, the branch is richer in lignin than the trunk and that in the latter the center is more lignified than the younger annual growths.

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[1] J. Ederer, G. P. 272036, (1913).

[2] R. Benedict and M. Bamberger, *Monatsh.*, **11** (1890), 260–267.

A similar series of methoxyl determinations was made on American species by Wheeler.[1]

Species	CH_3O, Per Cent
Persimmon (*Diospyros virginiana* L.)	4.02
Umbrella tree (*Magnolia tripetala* L.)	5.29
Sassafras (*Sassafras sassafras* (L.) Karst.)	5.03
Chinquapin (*Castanea pumila* (L.) Mill.)	4.45
Buttonwood (*Platanus occidentalis* L.)	4.59
Witch hazel (*Hamamelis virginiana* L.)	5.50
Pignut hickory (*Hicoria glabra* Britt.)	4.78
Sweet gum (*Liquidambar styraciflua* L.)	4.61
Dogwood (*Cornus florida* L.)	4.88
Honey locust (*Gleditsia triacanthos* L.)	5.09
Crabwood (*Gymnanthes lucida* Swartz)	6.08

The methoxyl content of the angiosperms will average somewhat higher than the gymnosperms, though the latter are higher in lignin.

Cellulose isolated by the chlorine method gives a methoxyl reaction. This is considered by some investigators as due to residual lignin, while Cross and Bevan[2] believe that CH_3O groups are characteristic of β-cellulose. Jute cellulose contains about 1.2 per cent methoxyl[3] in comparison with 4.6 per cent for jute. Since β-cellulose forms about 20 per cent of the jute cellulose, the methoxyl content of the β-cellulose would be 6.0 per cent. The methoxyl values of celluloses isolated by various methods are:[4]

Method	Oak, per cent	Fir, per cent
Tollens	0.28	0.43
König	0.49	0.68
Cross and Bevan	0.72	1.45
F. Schulze	2.50	2.59
H. Müller	1.00	1.23

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[1] A. S. Wheeler, *Ber.* **38** (1905) 2168–2169.

[2] C. F. Cross and E. J. Bevan, "Cellulose" (1916), pp. 93–94.

[3] *L.c.*, p. 158.

[4] J. König and F. Hühn, "Bestimmung der Zellulose in Holzarten" (1912), p. 47.

Spruce lignin isolated by the Willstätter method contained about 14 per cent CH_3O, some being lost by hydrolysis. Lignin acids prepared by Lange's method of alkaline fusion gave by the Zeisel method 13.11 per cent CH_3O (13.55 per cent CH_3OH).[1]

Heuser[2] methylated lignin isolated from wood with hydrochloric acid (sp. gr. 1.2) by suspending 5 grams in 100 cubic centimeters of 10 per cent sodium hydroxide, and treating at 60° with 30 grams of dimethylsulphate. The original CH_3O content was thereby increased from 14.65 per cent to 20.65 per cent with a yield of 96 per cent. By repeated methylation the CH_3O content was raised to 26.29 per cent. Removal of the methoxyl by repeated heating in a sealed tube with hydrochloric acid gave a residue containing: C, 67.45 to 69.30 per cent; H, 4.16 to 4.50 per cent. Three methylations of this residue gave a methyllignin with 5.79 per cent CH_3O. Lignin rendered soluble by heating with caustic soda in an autoclave at 170° gave on methylation a product with 24.7 per cent CH_3O. Another sample of lignin containing 14.15 per cent methoxyl gave on repeated methylation a lignin with 26.05 per cent CH_3O. The methoxyl content of ligninsulphonic acid was in the same way increased from 13.07 to 25.43 per cent.[3]

The methoxyl content of lignins isolated by the use of strong mineral acids varies greatly between species, but there is more uniformity in the conifers than in the hardwoods. Lignin isolated from fir and beech with 72 per cent sulphuric acid contained 13.90 and 16.64 per cent methoxyl, respectively.[4] Beckmann[5] found the following:

	Picea excelsa, per cent	*Pinus silvestris,* per cent	*Acer negundo,* per cent	*Fagus silvatica,* per cent
Lignin (Willstätter)	29.90	29.83	26.14	22.36
CH_3O therein	15.77	15.70	16.46	19.49

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[1] T. von Fellenberg, *Biochem. Z.*, **85** (1918), 79.

[2] E. Heuser, R. Schmitt, and L. Gunkel, *Cellulosechemie*, **2** (1921), 81–86.

[3] E. Heuser and S. Samuelsen, *Cellulosechemie*, **3** (1922), 78.

[4] J. König and E. Rump, *l.c.*, p. 63.

[5] E. Beckmann *et al.*, *Biochem. Z.*, **139** (1923), 491.

The extensive series of analyses by Ritter and Fleck[1] show a great variation in the lignin content of woods and the methoxyl content of the lignins isolated by the use of 72 per cent sulphuric acid. Their results are given in the table below.

METHOXYL IN LIGNIN FROM SAPWOOD AND HEARTWOOD

Species	Lignin in		CH_3O in lignin	
	Sapwood, per cent	Heartwood, per cent	Sapwood, per cent	Heartwood, per cent
White ash	26.95	27.39	17.4	19.5
	27.39	28.38	20.0	18.3
Yellow poplar	23.08	22.19	25.2	26.4
	23.86	23.69	24.7	25.4
Black hickory	21.87	22.85	25.4	25.3
Red alder	25.87	25.68	20.4	20.1
	26.64	25.94	19.8	20.3
Bald cypress	35.01	33.06	12.4	11.9
	35.31	32.27	14.0	12.6
Eastern white pine	26.52	26.14	15.7	17.6
Yellow cedar	29.03	28.73	15.1	16.7
Southern white cedar	29.85	31.39	17.1	15.9
	32.14	32.42	16.2	15.7
Incense cedar	34.73	33.67	17.1	18.4

It had been found[2] that the isolated lignins of redwood and live oak contained approximately 18 per cent of methoxyl, but the above analyses show variations from 11.9 per cent in the case of bald cypress to 26.4 per cent in yellow poplar.

With conifers, 10 to 21 per cent of the methoxyl, and with hardwoods, 21 to 38 per cent of the methoxyl is not recovered in the isolated lignin.[3] While part of the loss of methoxyl is due to subsequent boiling of the diluted acid, as recommended by Mahood,[4] the results indicate that if the methoxyl is wholly associated with the lignin, the lignins vary in chemical composition or in the mode of the methoxyl linkage. Dore[1] found that in redwood the methoxyl groups were entirely associated with the lignin, while in live oak (*Quercus agrifolia*), containing 5.80 per cent CH_3O, 2.08 per cent of the methoxyl appeared to be differently associated or very loosely combined with the lignin.[2]

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[1] G. J. Ritter and L. C. Fleck, *J. Ind. Eng. Chem.*, **15** (1923), 1055.
[2] G. J. Ritter and L. C. Fleck, *J. Ind. Eng. Chem.*, **14** (1922), 1050.
[3] G. J. Ritter, *J. Ind. Eng. Chem.*, **15** (1923), 1264.
[4] S. A. Mahood and D. E. Cable, *J. Ind. Eng. Chem.*, **14** (1922), 933.

Western yellow pine and white oak when repeatedly heated with dilute alkali under pressure gave 63 per cent of their methoxyl as methyl alcohol. Using the Zeisel method, the remaining methoxyl could be accounted for in the residue from white oak, but not in the case of western yellow pine.[3] These results are in interesting agreement with those obtained by destructive distillation, wherein 62 to 63 per cent of the methoxyl was recovered as methyl alcohol.[4] This suggests that the same methoxyl groups in the wood yield the methyl alcohol by alkaline hydrolysis, and the methyl alcohol and methoxyl groups in products of destructive distillation.

If the methoxyl in wood is all combined with the lignin, and in the same way, the ratio of lignin to methoxyl in the residue from wood subjected to varying periods of chlorination should be the same as for the original wood. This appears to hold for basswood but not for tanbark oak (*Quercus densiflora*) and incense cedar.[5]

Von Fellenberg[6] believes that the methyl alcohol formed by treating wood with dilute alkali is derived from pectin, and that obtained with strong sulphuric acid from lignin. Support for König's view that there are two or more forms of lignin is found in the fact that some methyl alcohol is formed on heating with 18 per cent sulphuric acid, though no sharp line of hydrolysis is obtained on increasing the strength of the acid to 72 per cent. The distribution of the methyl alcohol in an ash tree 5 years old is given in the following table. The methyl alcohol in lignin I was determined by heating the wood with 40 per cent sulphuric acid, while 72 per cent acid was used for lignin II.

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[1] W. H. Dore, *J. Ind. Eng. Chem.*, **12** (1920), 475.

[2] W. H. Dore, *J. Ind. Eng. Chem.*, **12** (1920), 986.

[3] G. J. Ritter, *J. Ind. Eng. Chem.*, **15** (1923), 1264.

[4] L. F. Hawley and S. S. Aiyar, *J. Ind. Eng. Chem.*, **14** (1922), 1056.

[5] G. J. Ritter, *J. Ind. Eng. Chem.*, **15** (1923), 1264.

[6] T. von Fellenberg, *Biochem. Z.*, **85** (1918), 45–161.

Per cent methyl alcohol in dry substance

Part of plant	Wood				Bark			
	Pectin	Lignin I	Lignin II	Total	Pectin	Lignin I	Lignin II	Total
Root hairs	0.17	0.16	1.73	2.06				
Main root	0.12	0.27	2.56	2.95	0.25	0.06	0.34	0.65
Shoot 5 years old	0.14	0.51	3.69	4.34	0.52	0.11	1.02	1.65
Shoot 4 years old	0.16	0.58	3.67	4.41	0.59	0.11	0.94	1.64
Shoot 3 years old	0.16	0.56	3.78	4.50	0.65	0.17	1.16	1.98
Shoot 2 years old	0.17	0.51	4.00	4.68	0.80	0.18	1.07	2.05
Fresh leaves	0.41	0	0	0.41				
Fresh twigs and leaf stems	0.76	0.12	0.18	1.06				

The three parent substances producing methyl alcohol occur to much less extent in the main root and rootlets than in the portion above ground. The pectin methyl alcohol is low in the wood in comparison with the lignin methyl alcohol, but in the bark the former may attain 30 to 40 per cent of the total. The distribution of methyl alcohol in fir wood follows:

ANALYSIS OF FIR WOOD

	PER CENT
Total methyl alcohol	4.65
Methyl alcohol from pectin	0.11
Methyl alcohol from total lignin	4.54
Methyl alcohol from colored ortholignin	4.43
Methyl alcohol from colored ortholignin acid	0
Methyl alcohol from uncolored lignin	0.11
Pectin content	1.10
Colored ortholignin	31.27
Methyl alcohol content of colored ortholignin	16.10
Methyl alcohol content of colored ortholignin acid	0

The hydrolysis of the methoxyl groups in lignin takes place to only a limited extent in the suphite pulping process and in the hydrolysis of wood with dilute acid under pressure as conducted in the manufacture of ethyl alcohol.[1] Five grams of Willstätter's lignin heated with 30 cubic centimeters of 5.7 per cent hydrochloric acid at 150 to 160° for 2 hours gave, by repeating the process, a total of 14.83 per cent methyl alcohol, 2.19 per cent acetic acid, and 0.73 per cent acetone. Four hours of continuous heating under pressure gave about 13 per cent of methyl alcohol, while heating at atmospheric pressure gave only 2.56 per cent. The yield of acetone is proportional to that of methyl alcohol, the maximum obtained being 1 per cent.

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[1] E. HEUSER and H. SCHMELZ, *Cellulosechemie*, **1** (1920), 49–58.

Oxidation of Lignin.—One of the characteristic properties of lignin is the ease with which it is decomposed by oxidizing agents. With the exception of alkaline fusion, usually the only products of oxidation aside from carbon dioxide and water are the simple aliphatic acids.

Willstätter's lignin has a high degree of inflammability. Pine lignin, when subjected to a cold stream of oxygen containing 2 per cent of ozone, burned in 25 seconds.[1]

When oxidized with concentrated nitric acid Willstätter's lignin gave 20 per cent of oxalic acid. The yield decreased in the presence of catalyzers, such as ammonium vanadate and ferrous sulphate. On the other hand, with 25 per cent nitric acid the yield was only 4 per cent. This was raised to 17 per cent by the addition of ferrous suphate.[2]

Attempts to obtain aromatic acids having a constitutional relationship to lignin by the alkaline oxidation of the methyl ethers of lignin and ligninsulphonic acid gave negative results.[3] Methylated ligninsulphonic acid gave 18.57 per cent of oxalic acid, and lignin methyl ether 26.40 per cent of oxalic acid and 100.8 per cent of carbon dioxide. In terms of carbon, only a little more than half of the carbon was accounted for in the oxidation of methyllignin: 44.76 per cent as carbon dioxide and 10.69 per cent as oxalic acid. Since the volatile acids amounted to only 0.9 per cent, it is probable that other volatile products are formed.

König and Rump[4] oxidized the lignin and crude fiber of fir wood with hydrogen peroxide and ammonia, lime water having been added to retain the carbon dioxide formed. With lignin, formic acid was the principal volatile acid obtained, and with the crude fiber, acetic acid.

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[1] E. Erdmann, *Z. angew. Chem.*, **34** (1921), 313.

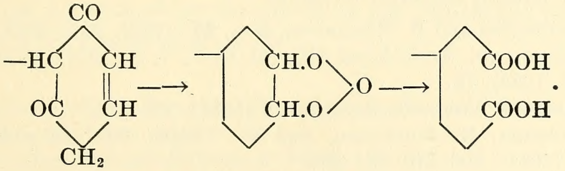
[2] E. Heuser, H. Roesch, and L. Gunkel, *Cellulosechemie*, **2** (1921), 13–19.

[3] E. Heuser and S. Samuelsen, *Cellulosechemie*, **3** (1922), 78–83.

[4] J. König and E. Rump, "Chemie—Pflanzen-Zellmembran," p. 61.

	Residue, per cent	Formic acid, per cent	Acetic acid, per cent	Carbon dioxide, per cent
Lignin....................	10.40	3.46	0.90	8.47
Crude fiber...............	66.19	4.24	16.07	8.43

Stutzer[1] tried without success to obtain benzene derivatives by treating the crude fiber of straw with a nitrating mixture (1 volume fuming HNO_3 and 2 volumes concentrated H_2SO_4). With this mixture, as well as by oxidation with nitric acid of sp. gr. 1.33, small amounts of oxalic, succinic, and suberic acids were obtained. König[2] worked with barium ligninsulphonate. He failed to obtain oxidation products bearing on the constitution of lignin by the use of potassium permanganate, electrolytic oxidation, hydrogen peroxide, ozone, and nitric acid. The chief products of oxidation were water, carbon dioxide, and oxalic acid; however, with ozone, formic acid, and with nitric acid, succinic acid, were also obtained. Lignin isolated from spruce wood with hydrochloric acid (1.21), when suspended in acetic acid and oxidized with nitric acid, gave a small amount of a pale-yellow, amorphous compound, $C_{19}H_{32}O_{14}N$. Lignin in suspension in acetic acid gave with ozone much greater amounts of oxalic acid than moist lignin, owing to moderation of the oxidation. The formation of an ozonide could not be confirmed by ultimate analysis and the use of semicarbazide acetate, the latter giving a very small amount of an amorphous precipitate.[3] This is contrary to the claim of Dorée and Cunningham[4] that an ozonide is formed from a keto-R-hexene ring.



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[1] A. Stutzer, *Ber.*, **8** (1875), 575–576.

[2] F. König, *Cellulosechemie*, **2** (1921), 105, 117.

[3] F. König, *Cellulosechemie*, **2** (1921), 117.

[4] C. Dorée and M. Cunningham, *J. Chem. Soc.*, **103** (1913), 677.

The formation of formic, acetic, oxalic, malonic, and succinic acids by the oxidation of lignin with hydrogen peroxide is considered as supporting the theory that lignin contains a coniferyl or vanillyl nucleus, succinic acid being also obtained by the oxidation of vanillin.[1]

Hägglund[2] fused Willstätter's lignin with caustic potash, with and without lead peroxide, obtaining a trace of formic acid but no acetic or oxalic acid. Catechol could not be detected but reactions were obtained for protocatechuic acid. Oxidation with alkaline potassium permanganate, and with nitric acid, with and without potassium chlorate, gave acetic acid but no oxalic acid.

Fischer[3] subjected lignin to pressure oxidation in the presence of caustic soda, obtaining benzene carboxylic acids. Since cellulose under the same conditions gave furan derivatives, he concludes that lignin has a benzenoid constitution. Willstätter's lignin, on oxidation by shaking with air at 200° in the presence of 2.5*N* sodium hydroxide for 40 hours, gave small amounts of mellitic acid, benzene pentacarboxylic acid, and oxalic acid.[4] Lignin dissolved in dilute sodium carbonate and oxidized at 200° with air at 55 atmospheres' pressure gave 8.28 per cent of aliphatic acids, and 3.12 per cent of benzene carboxylic acids, including benzoic, isophthalic, phthalic, trimellitic, mellitic, hemimellitic, prehnitic, benzene tricarboxylic, benzene pentacarboxylic, succinic, oxalic, and fumaric.[5]

Since aromatic bodies might be formed during the isolation of the lignin with strong hydrochloric acid, pine wood that had been extracted with a mixture of alcohol and benzene was oxidized at 200° in a current of air at 55 atmospheres' pressure for a long time. There was obtained 0.83 per cent of benzene pentacarboxylic acid, based on the lignin in the wood, in comparison with 1.65 per cent from Willstätter's lignin.[6]

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[1] O. Anderzén and B. Holmberg, *Ber.*, **56** (1923), 2044–2048.

[2] E. Hägglund, *Arkiv Kemi Mineral. Geol.*, **7**, 8 (1918), 1–20; *Cellulosechemie*, **4** (1923), 73.

[3] F. Fischer, *Naturwissenschaften*, **9** (1921), 958–965.

[4] F. Fischer, H. Schrader, and W. Treibs, *Ges. Abhandl. Kenntnis Kohle*, **5** (1921), 200–210, 221–229.

[5] F. Fischer, H. Schrader, and A. Friedrich, *Ges. Abhandl. Kenntnis Kohle*, **6** (1921), 1–21.

[6] F. Fischer, H. Schrader, and A. Friedrich, *Ges. Abhandl. Kenntnis Kohle*, **6** (1921), 22–26.

Lignin when heated with 10*N* potassium hydroxide at 300° for 3 hours gave phenols, or phenol carboxylic acids, and a small quantity of adipic acid. Fusion of lignin with potassium hydroxide gave 14.9 per cent of substances soluble in ether, among which was protocatechuic acid.[1]

Lignin in the presence of 5*N* caustic soda and oxygen at ordinary temperature lost 9.4 per cent of its weight in 46 hours. In 1000 hours 1 gram of lignin absorbed 82 cubic centimeters of oxygen. The products of the oxidation were mainly humic acids, together with small amounts of carbon dioxide, formic, acetic, oxalic, succinic, isophthalic, and benzene pentacarboxylic acids.[2]

Since cellulose and cane sugar gave small amounts of benzene carboxylic acids in addition to furan carboxylic acids, and since the yield of benzene carboxylic acids from lignin was only 3 to 4 per cent, this evidence for a benzenoid structure for lignin is not weighty.

Nitration of Lignin.—Though readily nitrated, no definite nitro derivatives have been obtained from lignin. Phelps,[3] assuming that lignin had aldehydic properties, treated waste sulphite liquor with various aromatic amines. Bright-red condensation products were obtained with primary amines, and brown or black derivatives with other amines. Condensation took place in the amino group, since the diazo reaction was unobtainable. Various dyes were obtained on treating the condensation products with nitric acid, the latter apparently reacting with the lignin group. On treating sulphite liquor with nitric acid a dye (lignone yellow) was obtained that dyed silk and wool orange yellow. The lignin from spent soda liquor after treatment with nitric acid dyes wool brown.[4]

Nitro derivatives of ligninsulphonic acid from sulphite liquor are prepared by Oman[5] by the use of 50 per cent nitric acid at 30 to 40°, or with mixed acid at 30°.

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[1] F. Fischer and H. Tropsch, *Ges. Abhandl. Kenntnis Kohle*, **6** (1921), 271–278; *Ber.*, **56** (1923), 2418.

[2] H. Schrader, *Brennstoff-Chem.* **3** (1922), 161–167.

[3] E. B. Phelps, *U. S. Geol. Survey, Water-supply Paper*, **226**, Washington (1909); *cf.* W. O. Walker, *J. Soc. Chem. Ind.*, **32** (1913), 390.

[4] M. P. Cram, *J. Ind. Eng. Chem.*, **6** (1914), 896.

[5] E. Oman, E. P. 103651, 103652 (1917).

Nitrolignin was prepared by treating 150 grams of Willstätter's lignin, with cooling, with 1000 cubic centimeters of $5N$ nitric acid, then warming until the product became uniformly orange colored. The yield was 60 per cent. The yellow powder, after solution in alcohol and precipitation with dry hydrogen chloride, had the composition $C_{42}H_{37}O_{24}N_3$. It contained three methoxyl and six hydroxyl groups. Acetylation yielded a tetracetyl derivative. Lignin, owing to its easy nitration, was regarded as having a phenolic structure.[1]

Lignin isolated from flax and wood with caustic soda, and having the formula $C_{40}H_{30}O_6.(OCH_3)_4.(OH)_5.CHO$, is readily nitrated with nitric acid alone or with an equal part of sulphuric acid at $-5°$. The resulting red powder is a trinitro derivative behaving as an aromatic compound. It is easily acetylated.[2]

A nitroso derivative is formed by dissolving 100 grams of sodium ligninsulphonate, obtained by the addition of sodium chloride to sulphite liquor, in 600 cubic centimeters of water and adding 60 grams of sodium nitrite in 100 cubic centimeters of water. After cooling with ice there is added 60 grams of concentrated sulphuric acid in 400 cubic centimeters of water. When the mixture has stood for several hours, the nitroso compound is precipitated with sodium chloride and washed with a strong solution of the same.[3]

When sodium ligninsulphonate is added to diazotized aromatic amines, brown to red dyestuffs are obtained.[4] Diazotized aniline, benzidine, and β-napthylamine-disulphonic acid give, respectively, brick-red, brown, and red products.

Distillation of Lignin.—The methyl alcohol and most of the acetic acid obtained on distilling wood were considered by Fremy and Urbain[5] as derived from the lignin, since lignin (vasculose) on distillation gave methyl alcohol.

Lignin prepared from spruce by the Willstätter method has been subjected to destructive distillation by several investigators.

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[1] F. Fischer and H. Tropsch, *Ges. Abhandl. Kenntnis Kohle*, **6** (1921), 279–288; *Chem. Centr.*, **94,** III (1923), 1639.

[2] W. J. Powell and H. Whittaker, *J. Chem. Soc.*, **125** (1924), 357; **127** (1925), 132.

[3] E. Oman, E. P., 103653, 103654 (1917).

[4] E. Oman, E. P., 103479, 103480; *cf.* 103822 (1917).

[5] E. Fremy and Urbain, *Compt. rend.*, **94** (1882), 110.

	Hägglund,[1] per cent	Heuser,[2] per cent	
CO_2	23	9.60	By volume
CO	17	50.90	
CH_4	12.5	37.50	
C_nH_{2n}	1.4	2.00	
H_2	13.6		
O_2	2.5		
N (and undetermined)	30.0		
Tar	9.6	13.00	By weight on the dry, ash-free lignin
Methyl alcohol	0.7	0.90	
Acetone	0.1	0.19	
Acetic acid	0.6	1.09	
Charcoal	45	50.64	

[1] E. Hägglund, *Arkiv Kemi, Mineral. Geol.*, 7, 2 (1918), 19.

[2] E. Heuser and C. Skiöldebrand, *Z. angew. Chem.*, **32** (1919), 41.

The discrepancy in the results may be due to different experimental conditions, and the probability that Hägglund's lignin, owing to its high furfural content (3.69 per cent), was not free from carbohydrates. In the light of Heuser's results in particular, lignin, in comparison with spruce wood, gives larger amounts of methane, carbon monoxide, charcoal, and tar, and less carbon dioxide. During distillation the methoxyl groups appear to be largely decomposed into gases, since the yield of methyl alcohol from the lignin is only about one-third of that of the original wood. The low yield of acetic acid is due in part to saponification of the acetyl groups during the isolation of the lignin. The lignin, the reaction being exothermic, began to char at 270° and decomposed to the greatest extent at 400 to 450°, though gases were formed up to 627°.

Lignin gives about one-half as much tar and nearly twice as much coke on distillation as does cellulose.[1] The lignin tar contained 50 per cent of acid and 13 per cent of neutral bodies, in comparison with 17 and 31 per cent, respectively, for the cellulose tar. Erdmann,[2] on distilling lignin from Scotch pine, obtained 18.1 per cent of tar containing 37 per cent of creosote. The total yield of creosote based on the lignin was 7.6 per cent. Both cellulose and lignin gave phenols on distillation, the latter, however, seven to eight times as much as the former. In the distillation water from lignin, a strong reaction for catechol was obtained, while in that from cellulose no catechol was detected.

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[1] F. Fischer and H. Schrader, *Ges. Abhandl. Kenntnis Kohle,* **5** (1920), 106–116.

[2] E. Erdmann, *Z. angew. Chem.*, **34** (1921), 309.

Pictet and Gaulis[1] distilled lignin from fir wood at 350 to 390° under 25-millimeters pressure, obtaining 15 per cent of tar. On removing the acids and phenols, 2 per cent of the lignin was obtained as a brown oil. The latter was separated into saturated and unsaturated hydrocarbons by means of liquid sulphur dioxide and fractioned. The third, sixth, and eighth fractions appeared to be identical with corresponding coal-tar fractions. The compound $C_{13}H_{16}$, which is similar to the hexahydrofluorene from coal tar, gave a tetrabromo-derivative, $C_{13}H_{12}Br_4$; m.p. 193°.

Fraction No.	Boiling point	Formula	Specific gravity	Refractive index
1 unsaturated	235–240°	$C_{13}H_{26}$	0.8091	1.4468
2	260–270	$C_{14}H_{26}$	0.8138	1.4532
3	270–280	$C_{16}H_{30}$	0.8218	1.4541
4	315–320	$C_{24}H_{44}$	0.8579	
5	Above 320	$C_{30}H_{60}$		
6 saturated	200–210	$C_{11}H_{16}$	0.8964	1.5119
7	230–240	$C_{12}H_{16}$	0.9172	1.5226
8	250–260	$C_{13}H_{16}$	0.9372	1.5422

The fifth fraction was identified as melene,[2] $C_{30}H_{60}$; m.p. 62 to 63°. Eugenol, m.p. 68°, was identified in the phenol fraction. The assumption that all the above fractions belong to the hydroaromatic series and that lignin contains a hydroaromatic ring seems hardly justified in view of the fact that the hydrocarbons represent but 2 per cent of the lignin distilled.

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[1] A. Pictet and M. Gaulis, *Helvetica Chim. Acta*, **6** (1923), 627–640.

[2] Melene, though formerly considered to be an alkylene hydrocarbon, is held by Pictet (*Ber.*, **48** (1915), 933) to be a cyclic, saturated compound.

There is no close relationship between lignin and cellulose, since on distillation under reduced pressure no lævoglucosan is obtained.[1]

Lignin on distillation with zinc dust gives about 17 per cent of a viscous oil distilling between 66 and 280° at 2-millimeters pressure. All of the fractions contain methoxyl.[2]

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[1] F. Fischer and H. Tropsch, *Naturprodukte*, **24** (1923), 8; *Ber.*, **56** (1923), 2418.

[2] P. Karrer and B. Bodding-Wiger, *Helvetica Chim Acta.*, **6** (1923), 817–822.

CHAPTER IV

COLOR REACTIONS OF WOOD

Wood gives a large number of color reactions with various inorganic and organic compounds. A few of the reactions are specific for lignin, while the majority are due to the presence of traces of aldehydes, adsorption, and other phenomena.

Color Reactions of Wood with Inorganic Compounds.—Potassium permanganate is rapidly reduced by lignocelluloses with the deposition of brown hydrated manganese dioxide. The extent to which fibers turn brown has been employed as a criterion of their technical value.[1] The greenish color obtained with ferric chloride is evidently due to traces of tannin. A 15 to 40 per cent solution of cobalt sulphocyanate colors lignified membranes blue, the phenomenon being apparently due entirely to adsorption. Casparis[2] considers this reaction more sensitive than the Mäule, or the phloroglucinol reaction.

Zinc chloriodine solution, which gives a yellow color with lignified tissues, is much used for staining wood pulp. Schorger[3] has found, however, that moist gelatinized wood is instantly stained a deep blue black. Sections of wood after boiling in water are also stained blue.[4]

In 1893, Cross and Bevan[5] found that lignocelluloses react with a ferricferricyanide solution to form Prussian blue, which is intimately attached to the fiber. The reaction is considered to take place specifically between the fiber and the ferricferricyanide solution, since lignocellulose has little action on ferric chloride or potassium ferricyanide solution taken separately.

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[1] A. Aisslinger, "Beiträge zur Kenntnis wenig bekannter Pflanzenfasern," Diss. Zürich (1907), p. 13.

[2] P. Casparis, *C. A.*, **15** (1921), 1333.

[3] A. W. Schorger, *J. Ind. Eng. Chem.*, **15** (1923), 814.

[4] M. C. Potter, *Ann. Botany*, **18** (1904), 121.

[5] C. F. Cross and E. J. Bevan, *J. Soc. Chem. Ind.*, **12** (1893), 104–106; "Cellulose," (1916), pp. 124–131.

Aldehyde groups in the lignocellulose are believed to be the cause of the reaction, though the presence of oxidizing agents does not prevent the formation of the blue precipitate. The reaction is not specific for lignin, since it is given by raw cotton. Haller[1] found that the pigment was deposited only in the cuticular layers and attributes the reaction to phenolic hydroxyl groups. Hydrocellulose and oxycellulose were without action. According to Crocker,[2] the reaction is obtained with any amine or phenol and with inorganic reducing agents. No reaction was obtained with benzaldehyde and formaldehyde.

The soft tissues of sections of wood treated momentarily with ferric sulphate, then washed with water, dilute acetic acid, and water, when immersed in potassium ferrocyanide are colored blue. The color is accentuated by the addition of a drop of hydrochloric acid. Devaux[3] considered this to be a specific reaction for pectin, an iron pectate being first formed. Lignified tissues are only weakly colored until after they have been subjected to the action of potassium hypochlorite, when they are strongly colored, due to the formation of oxycellulose.[4] Mangin[5] found that the middle lamella of wood cells, especially after treatment with alcohol-hydrochloric acid, was stained by ruthenium red. He also believed the latter to be a specific reagent for pectin, and that the middle lamella consists mainly of this substance.

Wood on treatment with chlorine becomes yellow, due to a combination of the chlorine with the lignin; if a dilute solution of sodium sulphite is applied, as in the Cross and Bevan method for determining cellulose, the liquid is colored pink to purple red.[6] The angiosperms give a more intense color than the gymnosperms. Payen[7] as long ago as 1849 observed that if various fibers were immersed for a short time in a saturated chlorine solution and then treated with ammonia, colorations were obtained; hemp, *e.g.*, gave a bright red.

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[1] R. Haller, *Färber-Ztg.*, **26** (1915), 157, 173; **30** (1919), 29, 43.

[2] E. C. Crocker, *J. Ind. Eng. Chem.*, **13** (1921), 625.

[3] H. Devaux, *Actes Soc. Linn. Bordeaux*, **6** (1901), XXXIII–XXXV.

[4] H. Devaux, *Actes Soc. Linn. Bordeaux*, **6** (1901), LVIII–LIX.

[5] L. Mangin, *Compt. rend.*, **116** (1893), 653.

[6] E. J. Bevan and C. F. Cross, *Chem. News*, **42** (1880), 80; C. S. Webster, *J. Chem. Soc.*, **43** (1883), 25.

[7] A. Payen, *Compt. rend.*, **29** (1849), 493.

A reaction having the same fundamental principle of oxidation was described by Mäule.[1] Lignified material when left in a 1 per cent solution of potassium permanganate for 5 minutes, washed, treated with dilute hydrochloric acid, washed, and then subjected to the action of ammonia, acquired a deep-red color. The writer[2] found that the angiosperms gave the typical red color, while the gymnosperms gave only an indefinite brownish gray. The Mäule reaction was applied by Sharma[3] to 40 species of angiosperms and 27 species of gymnosperms; with the latter a red color was in no case obtained, the reaction thus serving to distinguish between the woods of the two botanical subdivisions. An important earlier paper had been overlooked. De Lamarlière[4] studied the Mäule reaction in 1903 and found that a red color was never obtained with gymnosperms. He attributed the reaction to oxidized lignin, having observed that the intensity of color obtained with the Mäule reaction increased, while that with phloroglucinol decreased with the rigor of the oxidation; hence the two reactions were not identical. Fuming nitric acid and potassium hypochlorite did not give as good results as potassium permanganate. A 5 per cent solution of chromic acid acting for 5 minutes was just as effective, but Hoffmeister's reagent ($KClO_3 + HCl$) when rich in free chlorine was the best. He found that in the Mäule reaction the hydrochloric acid could be replaced by sulphuric or phosphoric acid, and the ammonia by potassium carbonate and other alkalis. This shows the close relationship between the Mäule reaction and the chlorine-sodium sulphite reaction, sodium sulphite being weakly alkaline. Recently, Casparis[5] and Crocker[6] reached a similar conclusion.

A tedious lignin reaction has been described by Combes.[7] The material is treated with a hypochlorite solution for 15 minutes, washed, heated on the water bath for 15 minutes with 1 gram of zinc oxide (or lead nitrate or acetate), suspended in 30 cubic centimeters of water, washed, treated with hydrogen sulphide for 10 to 15 minutes, and finally with a few drops of sulphuric acid. There results a fine red color changing to orange-red, and finally to brown in 8 to 10 hours.

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[1] C. Mäule, *Fünfstuck's Beiträge z. wiss. Botan.*, **4** (1900), 166.
[2] A. W. Schorger, *J. Ind. Eng. Chem.*, **9** (1917), 561.
[3] F. D. Sharma, *J. Forestry*, **2** (1922), 476–478.
[4] L. G. de Lamarlière, *Rev. gén. botan.*, **15** (1903), 149–159.
[5] P. Casparis, *l.c.*
[6] E. C. Crocker, *l.c.*
[7] R. Combes, *Bull. Sci. pharmacol.*, **13** (1906), 293–296.

Some of the inorganic acids give green colorations. Stolba[1] noticed that if a softwood was moistened with dilute sulphuric acid, it became after some time a beautiful moss green, the color being destroyed by water or alkalis. Concentrated hydrochloric acid also colors wood green.[2] The intense green color given wood by fuming hydrobromic acid is more permanent than that given by fuming hydrochloric acid and compares with the phloroglucinol reaction in delicacy.[3] Linde[4] found that sections of dry coniferous wood when placed in sulphuric acid (65 per cent) acquire a yellow color changing to green; if then placed in water the color changes to blue, finally becoming colorless. If the wood is first treated with a 5 per cent solution of caustic soda, the acid produces only a grayish-brown or gray color. The coloration produced by the acid varies with its strength and the species of wood, some woods giving only a yellow color. Old bast cells of a stem or root of conifers and cycads acquire a fine rose color when moistened with a drop of concentrated hydrochloric acid.[5] According to Guillard,[6] the coloration is obtained not only with bast and cork cells but with the structural elements of wood as well. The reaction has been attributed to the presence of coniferin.

Vanadium pentoxide dissolved in phosphoric acid stains wood a yellowish brown and gives a reddish-brown precipitate with vanillin.[7] Removal of the wood gum increases the intensity of the stain. Addition of vanadium pentoxide to the wood does not prevent staining with phloroglucinol.

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[1] F. Stolba, *J. prakt. Chem.*, **90** (1864), 466.

[2] H. Warnecke, *Pharm. Ztg.*, **33** (1888), 574.

[3] P. Friedländer, *Papier-Zeit.*, **25** (1900), 1877; H. Seidel, *Mitt. k.k. techn. Gewerbe-Mus.*, **10** (1900), 37–38.

[4] O. Linde, *Arch. Pharm.*, **244** (1906), 57–62.

[5] P. van Tieghem, *Compt. rend.*, **56** (1863), 963–965.

[6] A. Guillard, *Compt. rend.*, **56** (1863), 1126–1128; F. von Höhnel, *Akad. Wiss. Wien*, **76,** I (1877), 676; see *Ibid.*, p. 693 for older literature.

[7] J. Grüss, *Ber. botan. Ges.*, **38** (1920), 361–368.

Color Reactions of Wood with Organic Compounds.—A large number of color reactions with various organic bodies have been recorded; compounds containing amino and phenolic groups are the most important. A high intensity of color is usually obtained at once with the amines, while with the phenols light is of great assistance in bringing out the color.

In 1834, Runge[1] found that spruce wood, or a substance extractable therefrom with water and alcohol, gave a blue color when treated with a mixture of phenol and hydrochloric acid. It was later found that the reaction was not limited to coniferous woods, and that any of the common inorganic acids, but not organic acids, could be used in place of hydrochloric acid.[2] While concentrated hydrochloric acid alone may give a green color, this is not true of all woods; in the majority of cases the coloration is much more intense in the presence of phenol.

Von Höhnel,[3] in 1877, found that if an aqueous or alcoholic extract of cherry wood was applied to lignified tissues, then moistened with hydrochloric acid, a red to violet color was produced. The body causing the color was called *xylophilin.* Wiesner[4] considered *xylophilin* to be a mixture of phloroglucinol and a little catechol, and attributed the reaction mainly to phloroglucinol. He found that a 0.5 per cent solution of phloroglucinol, followed by hydrochloric acid, colored red even a trace of woody fiber. The color varies from cherry red to reddish violet.

The colorations given by various phenols and phenol ethers in the presence of hydrochloric acid are:

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[1] F. F. Runge, *J. prakt. Chem.*, **1** (1834), 24.

[2] R. von Wagner, *J. prakt. Chem.*, **51** (1850), 95.

[3] F. von Höhnel, *Akad. Wiss. Wien*, **76**, I (1877), 663–716.

[4] J. Wiesner, *Akad. Wiss. Wien*, **77**, I (1878), 60–66; *Dinglers polytech. J.*, 227 (1878), 397.

COLOR REACTIONS OF WOOD WITH PHENOLS

Reagent	Color	Author
Pyrogallol	Greenish blue	Wiesner[1]
Catechol	Bluish violet	Wiesner[1]
Resorcinol	Bluish violet	Wiesner[1]
Salicylic acid	Green	Warnecke[2]
Orcinol	Bluish violet	Von Lippmann[3]
α- and β-Napthol	Bluish green	Schaeffer[4]
Thymol	Bluish green	Molisch[5]
Guaiacol	Yellowish green	Czapek[6]
Cresol	Greenish	Czapek[6]
Anisol	Greenish yellow	Czapek[6]
Anethol	Greenish yellow	Czapek[6]
Hydroquinone	Green	Warnecke[2]

[1] J. WIESNER, cited by V. Grafe, *Monatsh.*, **25** (1904), 990; *cf.* F. VON HÖHNEL, *Akad. Wiss. Wien*, **76**, I (1877), 716.

[2] H. WARNECKE, *Pharm. Ztg.*, **33** (1888), 574.

[3] E. O. VON LIPPMANN, cited by Grafe, *l.c.*

[4] L. SCHAEFFER, *Ber.*, **2** (1869), 91; A. IHL, *Chem. Ztg.*, **9** (1885), 226.

[5] H. MOLISCH, *Ber. botan. Ges.*, **4** (1886), 303–305.

[6] F. CZAPEK, *Z. physiol. Chem.*, **27** (1899), 147.

The addition of potassium chlorate to the hydrochloric acid used with the phenol has been observed to hasten the color reaction. The Tommasis[1] found that by means of a pine splinter moistened in a solution consisting of 50 cubic centimeters of hydrochloric acid, 50 cubic centimeters of water, and 0.2 gram of potassium chlorate, it was possible to detect 1 part of phenol in 6000 parts of water.

Wood treated with pyrogallol in dilute glycerine solution and sulphuric acid, or zinc chloride, gives a violet color stable to water and hot alcohol.[2] Pure phenol ethers, such as anethol and anisol, do not color wood at all;[3] a coloration with these compounds is without doubt due to the presence of traces of phenol.

The inorganic salts of organic bases give yellow, green, and red stains. Runge[4] was the first to notice that aniline sulphate colored wood yellow. This reagent was subsequently proposed by Schapringer[1] for the detection of wood pulp in paper and by Wiesner[2] for determining lignification in plant anatomy.

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[1] T. and D. TOMMASI, *Ber.*, **14** (1881), 1834–1836; F. VON HÖHNEL and H. MOLISCH, *l.c.*

[2] C. REICHL, *Rep. anal. Chem.*, **3** (1883), 125.

[3] E. C. CROCKER, *J. Ind. Eng. Chem.*, **13** (1921), 625; O. ADLER, *Biochem. Z.*, **128** (1922), 32.

[4] F. F. RUNGE, *Pogg. Ann.*, **31** (1834), 65.

The colorations obtained with various amino derivatives are listed on the following page.

According to Crocker, no color is obtained with formamide, acetamide, urea, or acetanilid.

Wood suspended in dilute soda solution is colored a brick red by the addition of a very small amount of diazobenzene chloride. Some of the hardwoods do not react.[3]

The reaction between dimethyl-*p*-phenylenediamine and wood is not a definite one.[4] The intensities of the colorations and the amounts of the base fixed, when wood flour was treated with increasing proportions of this base in equal volumes of water, were proportional to the quantities of the base taken, an equilibrium being reached. This reagent should be used with caution for the detection of lignified fibers, particularly in paper, since it reacts very readily with oxidizing agents, such as ozone, chlorine, and peroxides, a red color being produced.[5] The red color produced with wood is discharged by a drop of ammonia and restored by glacial acetic acid, while if the color has been produced by chlorine it remains permanently discharged by this treatment.

Paranitraniline, 0.2 gram in 100 grams of 20 per cent sulphuric acid, colors lignin a reddish orange.[6] Wheeler[7] states that a 2 per cent solution of the nitranilines in 12 per cent hydrochloric acid gives a blood-red color, the *p*-compound being the most sensitive. According to Grandmougin,[8] *p*-amido-diphenylamine gives a Bordeaux red, resistant to acids, and much more sensitive than *p*-nitraniline. If the amino groups are diazotized or methylated, the coloring power is greatly reduced or destroyed.[9] It

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[1] S. Schapringer, *Dinglers polytech. J.*, **176** (1865), 166.

[2] F. Wiesner, *Karsten's bot. Untersuchungen*, **1** (1866), 120.

[3] E. Ungar, Diss. Budapest (1916), p. 49.

[4] C. F. Cross, E. J. Bevan, and J. F. Briggs, *Ber.*, **40** (1907), 3119.

[5] C. Wurster, *Papier-Zeit.*, **28** (1903), 1608–1609.

[6] A. Bergé, *Bull. Soc. Chim. Belg.*, **20** (1906), 158–159.

[7] A. S. Wheeler, *Ber.*, **40** (1907), 1888–1890.

[8] E. Grandmougin, *Ber.*, **40** (1907), 2453.

[9] E. Grandmougin, *Z. Farben-u. Textilchemie*, **5** (1906), 321–323.

COLOR REACTIONS OF WOOD WITH ORGANIC BASES

Reagent	Color	Author
p-Toluidine	Yellow	Singer[1]
o-Toluidine	Yellow	Covelli[2]
Benzidine	Yellow to red	Dukelsky[3]
p-Aminobenzylidenacetophenone	Brownish red	Rupe[4]
o-Bromphenetidine	Yellow	Piutti[5]
o-Bromanisidine	Yellow	Piutti[5]
o- and *p*-Amidophenol	Yellow	Piutti[5]
p-Anisidine	Yellow	Piutti[5]
p-Phenetidine	Yellow	Piutti[5]
m- and *p*-Phenylaminophenol	Yellow	Piutti[5]
Aminoanthracene	Blood red	Kielmeyer[6]
Morphine	Green	Warnecke[7]
Acetanilid	Green	Warnecke[7]
Phenacetin	Green	Warnecke[7]
Xylidine	Yellow	Nickel[8]
α- and β-Napthylamine	Yellow	Nickel[8]
m-Phenylenediamine	Yellow	Molisch[9]
p-Phenylenediamine	Orange red	Covelli[10]
Dimethyl-*p*-phenylenediamine	Red	Wurster[11]
Toluylenediamine	Dark orange	Hegler[12]
Diphenylamine	Golden orange	Ellram[13]
Urea	Yellow	Ihl[14]
Antipyrine	Red	Ihl[14]
Phenylhydrazine	Yellow, then green	Nickel[15]
p-Amidodiphenylamine	Bordeaux red	Grandmougin[16]
Hydrazine	Yellow to orange	Nickel[17]
Sulphanilic acid	Orange yellow	Covelli[18]
o-, *m*-, and *p*-Chloraniline	Orange yellow	Covelli[18]
o- and *p*-Aminophenol	Orange yellow	Covelli[18]
Orthoform	Orange yellow	Covelli[18]
Aminosalicylic acid	Orange yellow	Covelli[18]
o- and *p*-Aminobenzoic acid	Orange yellow	Covelli[18]
o- and *m*-Nitraniline	Orange red	Covelli[18]
p-Nitraniline	Reddish orange	Covelli[18]
Triaminophenol	Orange red	Covelli[18]

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[1] M. SINGER, *Monatsh.*, **3** (1882), 408.

[2] E. COVELLI, *Chem. Ztg.*, **25** (1901), 684.

[3] S. DUKELSKY, *Papier-Fabr.*, **10** (1912), 6; H. SCHNEIDER, *Z. wiss. Mikrosk.*, **31** (1914), 68.

[4] H. RUPE and A. PORAI-KOSCHITZ, *Z. Farben-Ind.*, **5** (1906), 317.

[5] A. PIUTTI, *Gazz. Chim. Ital.*, **28,** II (1898), 168–170.

[6] E. KIELMEYER, *Dinglers polytech. J.*, **227** (1878), 584–558.

[7] H. WARNECKE, *Pharm. Ztg.*, **33** (1888), 573.

[8] E. NICKEL, "Die Farbenreaktionen der Kohlenstoffverbindungen" (1890), p. 51.

[9] H. MOLISCH, *Sitzb. zoöl. botan. Ges. Wien*, **37** (1887), 30.

[10] E. COVELLI, *Chem. Ztg.*, **25** (1901), 684; H. BLAU, *Pharm. Post*, **38** (1905), 753.

[11] C. WURSTER, *Ber.*, **20** (1887), 808–810.

[12] R. HEGLER, *Flora*, **73** (1890), 35.

[13] W. ELLRAM, *Chem. Centr.*, **II** (1896), 99.

[14] A. IHL, *Chem. Ztg.*, **13** (1889), 831.

[15] E. NICKEL, *Chem. Ztg.*, **17** (1893), 1209; E. SENFT, *Monatsh.*, **25** (1904), 419; O. ADLER, *Biochem. Ztg.*, **128** (1922), 32.

[16] E. GRANDMOUGIN, *Ber.*, **40** (1907), 2453.

[17] E. NICKEL, *Chem. Ztg.*, **17** (1893), 1243.

[18] E. COVELLI, *l.c.*

had been found by Covelli[1] that if one of the hydrogen atoms in the amino group is replaced by alkyl or phenyl groups, the amine retains the power of coloring wood, but to a less degree; however, it vanishes on introducing an acid radical. Wood treated with phenylhydrazine hydrochloride becomes yellow, then red, and finally green. If the wood has been given a preliminary treatment with chlorine, it is no longer colored by amines. The change in color of the amine condensation products may be due to phototrophy. Among the anils studied by Senier and Shepheard,[2] salicylidene-*m*-toluidine changed from pale yellow to deep orange on exposure to sunlight, the change being reversible. The green color given by phenylhydrazine is considered by Jentsch[3] as more definite than the phloroglucinol red for determining the extent to which wood pulp has been freed from lignin.

Some of the aromatic bases with nitrogen in the ring give deep colorations with lignin. Runge[4] found that hydrochloric acid and pyrrol turned wood a dark purplish red. The reaction has been rediscovered several times.[5] It is a sensitive reagent for lignin, but has the disadvantage of decomposing readily.[6] Streeb[7] used α-methylindol and obtained a dark red with lignified material. According to Renker,[8] oxycellulose is also colored red by this reagent. A saturated solution of thalline sulphate (*p*-methoxytetrahydroquinoline sulphate, $(C_6H_{13}NO)_2.HSO_4 + 2H_2O$) colors lignin a dark orange yellow, while cellulose and cork are not colored.[9] The reagent is very sensitive and gives a coloration even in a 0.01 per cent solution. The red color given by pyrrol, indol, and carbazol is destroyed by ammonia.[10]

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[1] E. Covelli, *l.c.*

[2] A. Senier and F. G. Shepheard, *J. Chem. Soc.*, **95** (1909), 441–445; 1943–1955.

[3] S. Jentsch, *Z. angew. Chem.*, **31** (1918), 72.

[4] F. F. Runge, *J. prakt. Chem.*, **1** (1834), 24.

[5] N. Lubavin, *Ber.*, **2** (1869), 100; A. Ihl, *Chem. Ztg.*, **14** (1890), 304, 1571; M. Niggl, *Chem. Ztg.*, **15** (1891), 298.

[6] M. Singer, *Monatsh.*, **3** (1882), 398.

[7] E. Streeb, "Ueber Derivate des Lignin's," Diss. Göttingen (1892).

[8] M. Renker, "Bestimmungsmethoden der Cellulose," Berlin (1910), p. 26.

[9] R. Hegler, *Botan. Centralbl.*, **38** (1889), 616–618; *Flora*, **73** (1890), 31–61.

[10] E. Covelli, *Chem. Ztg.*, **25** (1901), 684.

Reagent	Color	Author
Bone oil	Red	Ihl[1]
Tobacco extract	Red	Ihl[2]
Pyridine	Pink	Ihl[3]
Picoline	Yellow	Ihl[3]
Lutidine	Yellow	Ihl[3]
Lepidine	Red	Ihl[4]
Skatol	Violet	Mattirolo[5]
Carbazol	Reddish violet	Mattirolo[5]
Indol	Cherry red	Niggl[6]

[1] A. Ihl, *Chem. Ztg.*, **14** (1890), 34.
[2] A. Ihl, *Chem. Ztg.*, **14** (1890), 67.
[3] A. Ihl, *Chem. Ztg.*, **14** (1890), 304.
[4] A. Ihl, *Chem. Ztg.*, **14** (1890), 1571.
[5] D. O. Mattirolo, *Z. wiss. Mikrosk.*, **2** (1885), 354–355.
[6] M. Niggl, *Flora*, **64** (1881), 545–547; *cf.* A. Baeyer, *Ann.*, **140** (1866), 296.

Crocker[1] states that carbazol and pyridine give no coloration.

Color reactions are also obtained by the use of aliphatic alcohols and sulphuric acid. When equal volumes of amyl alcohol, free from furfural, and sulphuric acid are heated at about 90° until evolution of gas begins, a reddish-yellow solution is obtained which stains wood fibers red to deep blue.[2] The color is attributed to furfural formed from xylose. Linde[3] states that the reaction is misleading since the same coloration is produced with asbestos. All the alkyl sulphuric acids and aryl sulphonic acids give a red or blue color with lignin; napthalene sulphonic acid gives a blue and anthracene sulphonic acid a deep-red color.[4] Benzene heated with sulphuric acid until sulphur dioxide is evolved gives an intense blue with wood. A reddish-violet color is obtained with isobutyl or hexyl alcohol, or isobutyl aldehyde and sulphuric acid in the presence of lignin; the reaction is not obtained with hydrochloric acid.[5]

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[1] E. Crocker, *l.c.*
[2] A. Kaiser, *Chem. Ztg.*, **26** (1902), 335.
[3] O. Linde, *Arch. Pharm.*, **244** (1906), 62.
[4] J. Hertkorn, *Chem. Ztg.*, **26** (1902), 632.
[5] V. Grafe, *Oesterr. botan. Zeits.*, **55** (1905), 174–176.

Thiophene[1] stains wood green and methylheptenone[2] red in the presence of hydrochloric acid. Reichl[3] found that egg albumin dissolved in dilute sulphuric acid to which a little ferrous sulphate was added, when heated, colored spruce shavings green, while the liquid became violet. Wood is colored violet when dipped into oil of myrrh,[4] partially dried, and then immersed in dilute hydrochloric acid; sesame oil[5] gives an intense green.

The various amines and phenols were found by Barrett[6] to be unsuited for the detection of lignified impurities in cotton to be used for nitration, preference being given to staining with malachite green. A solution is prepared by dissolving 0.1 gram of the dye in 100 cubic centimeters of hot water, diluting to 500 cubic centimeters, adding 50 cubic centimeters of 40 per cent formaldehyde solution, 1 gram of sodium bisulphate, and making up to 1 liter. A second solution consists of 20 grams of bleaching powder in 1 liter of water. The sample (3 grams) is heated with 300 cubic centimeters of the dye solution on the water bath for 10 minutes and then 25 cubic centimeters of the clear hypochlorite solution added with rapid stirring. After 5 minutes the sample is removed and washed. The ligneous impurities are stained, while the color on the cotton is completely discharged. Bugnon[7] treated lignified sections with sodium hypochlorite, washed, and then immersed them in a solution of light-green F. S. (sodium diethyl-dibenzyl-diamino-triphenylcarbinol-sulphonate) in 5 per cent hydrochloric acid. A permanent green color was obtained. Lignified tissues are stained a deep red by an aqueous solution of fuchsin; in distinction from non-lignified tissues, maceration in glycerine does not remove the color.[8]

The nature of the substances in lignified tissues producing the various color reactions is obscure. The phenol reaction was first attributed to the glucoside coniferin. In 1861, Hartig[1] discovered this compound in the cambium sap of *Larix europea* and called it "laricin." Kubel[2] gave coniferin its present name, having found it to be present in the cambium sap of all of the conifers examined. Coniferin, $C_{16}H_{22}O_8 + 2H_2O$, crystallizes in satiny needles that lose their water of crystallization at 100° and melt at 185°. It is very slightly soluble in cold water, readily so in hot, and insoluble in ether. On hydrolysis with emulsin it gives *d*-glucose and coniferyl alcohol; dilute acids on heating produce resinification; oxidation with chromic acid mixture gives vanillin. Coniferin and vanillin give a red color with phloroglucinol-hydrochloric acid.

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[1] A. Ihl, *Chem. Ztg.*, **14** (1890), 1707.

[2] E. and H. Erdmann, *Ber.*, **32** (1899), 1218.

[3] C. Reichl, *Monatsh.*, **11** (1890), 159.

[4] O. Linde, *Arch. Pharm.*, **244** (1906), 62.

[5] H. Kreis, *Chem. Ztg.*, **28** (1904), 956–957.

[6] F. L. Barrett, *J. Soc. Chem. Ind.*, **39** (1920), 81–82T.

[7] P. Bugnon, *Compt. rend.*, **168** (1919), 62–64.

[8] G. Dragendorff, "Plant Analysis," London (1884), p. 95.

Tiemann and Harmann[3] found that coniferin gives with concentrated sulphuric acid a dark-violet color, changing to blue on the addition of water. Concentrated hydrochloric acid in the cold gives no coloration, but on heating a blue precipitate is produced. The young wood of conifers, on moistening with concentrated sulphuric acid, is colored violet. Since coniferin and phenol with concentrated hydrochloric acid, in the sunlight, were almost instantly colored a deep blue, the bluish color obtained with phenol-hydrochloric acid and pine wood was attributed to traces of coniferin in the latter. Soon afterwards Tangl[4] applied the phenol reaction to angiosperms and, having obtained the same bluish green as with the conifers, decided that coniferin must be widely distributed in nature.

The characteristic "wood substance" was considered by Singer[5] to contain vanillin and coniferin, since the hot-water extract had the odor of the former and gave some of the color reactions of the latter. Lignin was looked upon as a mixture of several substances and not as a definite compound. He found that old, fine spruce sawdust had to be boiled with water for 18 days before it ceased to give a blue color with phenol-hydrochloric acid. Based on the slender evidence of odor or color reactions, various observers have reported the presence of vanillin in wood,[1] and in sulphite[2] and soda[3] liquor from the manufacture of wood pulp. Fresh linden bark[4] collected in summer contains detectable amounts of vanillin, though bark collected from the same tree during the winter months was free from it. The presence of vanillin in decayed oak wood[5] has been reported on the basis of the blue color obtained by the use of the phosphotungstic-phosphomolybdic acid solution of Folin and Denis.[6] The most trustworthy occurrence of vanillin is that mentioned by von Lippmann,[7] who found a sufficient deposit on a board to determine that it gave a blue color with ferric chloride and had a m.p. of 81°. It is possible that under certain pathological conditions vanillin might be formed from coniferin.

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[1] T. Hartig, *Jahrb. f. Forster*, **1** (1861), 263.

[2] W. Kubel, *J. prakt. Chem.*, **97** (1866), 243–246.

[3] F. Tiemann and W. Harmann, *Ber.*, **7** (1874), 608–623.

[4] E. Tangl, *Flora*, **57** (1874), 239.

[5] M. Singer, *Monatsh.*, **3** (1882), 395–410.

Since diphenylamine gave an intense greenish yellow with vanillin and a golden yellow with coniferin, Ellram[8] concluded that coniferin predominated in the membranes of the youngest cells, and vanillin in the oldest lignified tissues. Hegler[9] considered coniferin to be always present in lignified membranes; according to Richter,[10] the best reaction for wood substance is the test with phloroglucinol-hydrochloric acid and its cause is vanillin. Von Udránzky[11] found that the woods of *Pinus sylvestris, Abies excelsa,* and *A. pectinata* were colored yellow or greenish with concentrated hydrochloric acid in the cold, and reddish yellow, red, or bluish green on heating, the color being especially intensive at the border of the annual rings. Concentrated sulphuric acid, if washed off immediately to prevent charring, gave a bluish green. The color reactions obtained with sulphuric acid, with and without furfural, and several substances of possible occurrence in wood were studied. He concluded that, since strong acids produce furfural from wood, and since furfural gives a blue color with many compounds that might occur in wood, the reaction cannot be safely attributed to coniferin alone.

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[1] W. Hoffmeister, *Landw. Jahrb.*, **17** (1888), 260; V. Grafe, *Monatsh.*, **25** (1904), 1014.

[2] J. B. Lindsey and B. Tollens, *Ann.*, **267** (1892), 341; H. Seidel, *Z. angew. Chem.*, **11** (1898), 876; E. Pollacsek, *Oesterr. Privilegium*, 1524 (1898); *cf.* M. Müller, "Literatur der Sulfit-Ablauge," Berlin (1911), p. 109; F. König, *Cellulosechemie*, **2** (1921), 109.

[3] Anon., *Dinglers polytech. J.*, **216** (1875), 372.

[4] W. Braeutigam, *Pharm. Ztg.*, **45** (1900), 164; *Arch. Pharm.*, **238** (1900), 556.

[5] M. X. Sullivan, *J. Ind. Eng. Chem.*, **6** (1914), 919–921.

[6] O. Folin and W. Denis, *J. Ind. Eng. Chem.*, **4** (1912), 670.

[7] E. O. von Lippmann, *Ber.*, **37** (1904), 4521–4522.

[8] W. Ellram, *Chem. Centr.*, **II** (1896), 99.

[9] R. Hegler, *Flora*, **73** (1890), 46.

[10] O. Richter, *Z. wiss. Mikrosk.*, **22** (1905), 383.

[11] L. von Udránzky, *Z. physiol. Chem.*, **12** (1888), 352–376.

Substance	With furfural and sulphuric acid	With sulphuric acid only
Coniferin	Dark cherry red changing rapidly to violet	Same coloration
Vanillin	Violet, a green-colored ring below	Emerald green
Catechol	Violet color changing to brown	Weak green
Gallic acid	Light violet	No color

A step in advance was made by Nickel,[1] who attributed the "lignin" reactions to the aldehydic nature of wood; that these reactions were due to vanillin was very improbable, owing to the slight sensitiveness of vanillin, in comparison with wood, to phenols and aniline. It was found that wood behaved as an aldehyde towards Schiff's reagent (fuchsin + SO_2); wood impregnated with sodium bisulphite was not colored by aniline sulphate, and when treated with hydroxylamine did not react with phloroglucinol. Similar conclusions were reached by Seliwanoff.[2] Definite compounds are formed between lignin and phenols, and primary and secondary amines, but not tertiary amines; like an α-oxyaldehyde or α-oxyketone, wood reacts with phenylhydrazine with the evolution of ammonia.

In 1899, Czapek[3] isolated a substance which he named "hadromal" by digesting wood with strong stannous chloride solution and extracting the wet residue with benzene; when purified by conversion into the bisulphite compound and several crystallizations from petroleum ether, it formed a light-brown crystalline powder melting at 75 to 80°. It was not volatile in steam, but was sparingly soluble in hot water, and readily so in organic solvents. Hadromal had phenolic and aldehydic properties and gave the various lignin reactions to a high degree. The wood contained 1 to 2 per cent of the compound, which was apparently liberated from its combination with cellulose by the stannous chloride. The view of a chemical combination was supported by the arguments that cellulose cannot be easily extracted from wood by cuprammonium solution and it is not stained blue directly by iodine reagents.

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[1] E. Nickel, *Chem. Ztg.*, **11** (1887), 1520; *Botan. Centr.*, **38** (1889), 753–756.

[2] T. Seliwanoff, *Chem. Centr.*, **I** (1889), 549.

[3] F. Czapek, *Z. physiol. Chem.*, **27** (1899), 141–166.

Hadromal, according to Grafe,[1] consists of a mixture of vanillin, methylfurfural, and catechol; coniferin, to which is due the blue coloration with phenol, is also present in wood. Hadromal was prepared by the gentle digestion of wood with 10 per cent hydrochloric acid, and also by heating with water under pressure. The wood after extraction with alcohol was heated with water at 180° for 1 hour in a sealed tube from which the air had been removed. The sawdust after drying was extracted with benzene. The green-colored solution contained "hadromal" of the composition stated above. The resin extracted with alcohol gave the phloroglucinol reaction, and, judging from the depth of color for the extracted wood, at least half of the color-producing material in the wood was associated with the resin. The latter on digestion with concentrated hydrochloric acid became first yellow, then green like wood. The green color obtained on treating wood with concentrated hydrochloric acid or preferably hydrobromic acid was attributed to a condensation product of methylfurfural with coniferin,[2] though methylfurfural has never been detected in wood.

It should be mentioned that the "wound" resin (Ueberwallungsharz) of *Pinus laricio* Poir. was found by Bamberger[3] to give a strong color reaction with phloroglucinol. The resin contained dihydrocinnamic acid, caffeic acid, ferulic acid, and a small amount of vanillin, the two latter compounds at least being colored red by phloroglucinol. Ferulic acid gives a red color very similar to that obtained with lignin.[1] Besides vanillin, many cyclic and aliphatic aldehydes,[2] as well as ethereal oils or compounds containing allyl[3] groups, give a red coloration with phloroglucinol.

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[1] V. Grafe, *Monatsh.*, **25** (1904), 987–1029.

[2] V. Grafe, *l.c.*, p. 1029.

[3] M. Bamberger, *Monatsh.*, **12** (1891), 445; **15** (1894), 505.

Czapek[4] states that he has not found it possible to obtain a mixture of catechol, vanillin, and methylfurfural having the properties of hadromal; by the methods of obtaining hadromal employed by Grafe, oxidation may have taken place with the formation of vanillin and catechol. Small amounts of hadromal may be obtained by alcoholic extraction. On chemical and biological grounds, hadromal is probably related to coniferyl alcohol.

It was found by Potter[5] that boiling water or even cold water acting on wood for a long time extracted a substance giving the reactions of lignin with phloroglucinol and thalline sulphate. The extract obtained by heating Douglas fir and western hemlock sawdust with water in an autoclave gave only a faint pink with the phloroglucinol reagent, but the ether extract of the aqueous solution gave a decided red color.[6] Tests for coniferin with phenol and hydrochloric acid were negative.

The violet color obtained by von Höhnel by treating cherry wood with hydrochloric acid, and considered by Wiesner as due to the presence of phloroglucinol, is without doubt due to tannins. Von Wagner[7] found that coniferous wood was also colored violet by the acid if exposed to sunlight. Definite proof of the occurrence of phloroglucinol in plants appears to be wanting.[8] Votocek[9] states that the tannins in tea extract behave like phloroglucinol in that they give with furfural and dilute hydrochloric acid similar greenish-black, water-insoluble condensation products; with sufficiently concentrated acid, the extract colors wood a beautiful violet. Tannin extracts from willow, birch, oak, and other barks gave the same reaction. The violet color produced by various tannins, when a pine splinter is moistened with hydrochloric acid, has been explained through the presence of vanillin in the wood and phloroglucinol in the tannins.[1] Lauffmann,[2] from a series of experiments, concludes that the reaction is due neither to the presence of phloroglucinol in tannins nor to vanillin in wood.

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[1] F. Czapek, *Z. physiol. Chem.*, **27** (1899), 151; O. Tunmann, *Ber. botan. Ges.*, **30** (1912), 249.

[2] C. Hartwich and M. Winckel, *Arch. Pharm.*, **242** (1904), 462.

[3] K. Kobert, *Z. anal. Chem.*, **46** (1907), 711.

[4] F. Czapek, "Biochemie der Pflanzen," 2nd ed., **I** (1913), p. 691.

[5] M. C. Potter, *Ann. Botany*, **18** (1904), 121.

[6] H. Schmitz, *Ann. Missouri Botan. Gardens*, **6** (1919), 104.

[7] R. von Wagner, *Dinglers polytech. J.*, **228** (1878), 173.

[8] H. Moller, *Ber. pharm. Ges.*, **7** (1897), 344–352.

[9] E. Votocek, *Chem. Ztg.*, **37** (1913), 897.

Phloroglucinol is a delicate reagent for lignin; a drop of phloroglucinol solution as dilute as 1 part in 30,000 will produce a red spot on newsprint in 1 minute.[3] It is not infallible, however; Hancock and Dahl[4] found that the pith-like stem of *Æschynomene aspera,* though having the morphological characters of a true wood, gave only the faintest colorations with aniline salts and phloroglucinol. The wood contained 2.9 per cent of methoxyl, CH_3O, and gave 11.6 per cent of furfural. On chlorination, a yellow chloride was obtained that gave the characteristic deeply colored solution with sodium sulphite. Von Faber[5] found numerous instances where plant tissues were stained by phloroglucinol and not by the Mäule reaction, and *vice versa.* The former was considered to be a specific reagent for hadromal and the latter for lignin. Lignified fibers, particularly jute, after cooking with caustic soda and bleaching, frequently fail to be stained by amines and phenols, though the presence of lignin may be shown by the Mäule or the Cross and Bevan reaction. Renker[6] accordingly considers the latter as characteristic lignocellulose reactions, while the amines and phenols react only with traces of aldehydes in the fibers. Dark-brown, lignified tissues may sometimes mask the red color of phloroglucinol.[7]

Ground wood was found by Cross[8] and his associates to develop a maximum intensity of color when treated with 1 per cent of phloroglucinol in comparison with 10 per cent. Since the wood absorbed 6.7 per cent of phloroglucinol, it would appear that the color development represented but a small part of the reaction, and that, in the main, there is formed a definite lignin-phloroglucide compound that is colorless. Zechmeister[1] came to the conclusion that the lignin reaction is due to a small amount of an aromatic aldehyde combined with a larger group (carbohydrate); the coloration with aniline salts is quinonoid. The aldehyde probably does not exist in wood in amounts greater than a few hundredths of a per cent.[2] A very similar aldehyde, judging from spectroscopic investigations, occurs in clove and sassafras oils and is probably produced from lignified tissue during the distillation of the oils.

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[1] H. R. Procter, "Leather Industries Laboratory Book" (1908), 152, 158–163.

[2] R. Lauffmann, *Ledertech. Rundschau,* **11** (1919), 61–63.

[3] C. F. Cross, E. J. Bevan, and J. F. Briggs, *Ber.,* **40** (1907), 3121.

[4] W. C. Hancock and O. W. Dahl, *Chem. News,* **72** (1895), 16–18.

[5] F. C. von Faber, *Ber. botan. Ges.,* **22** (1904), 177–182.

[6] M. Renker, *Papier-Fabr.,* (1910), *Fest u. Auslandsheft,* 42.

[7] C. van Wisselingh, *Pharm. Weekblad,* **57** (1920), 77.

[8] C. F. Cross, E. J. Bevan, and J. F. Briggs, *Ber.,* **40** (1907), 3119–3126.

Ihl[3] thought that cinnamic aldehyde might be present in wood, since this aldehyde gave a yellow color with aniline sulphate, a red color with phloroglucinol, and behaved like lignin with most reagents. The differences in color obtained with different woods using hydrazine sulphate, and the variations from the colors given by cinnamic aldehyde and vanillin, led Nickel[4] to point out the unsoundness of drawing conclusions from color reactions; piperonal, *p*-hydroxybenzaldehyde, and salicylic aldehyde gave similar colorations. According to Wocker,[5] vanillin or a related aromatic oxyaldehyde is present in lignin, since wood and vanillin give the same intensive yellow with benzididine chloride. The reaction takes place with lignin with great rapidity. Hydroxyfurfural[6] or a closely related body has also been fixed upon as the active agent. The assumption of Klason[7] that coniferyl aldehyde is responsible for the color reactions has only a hypothetical basis.

The intense and rapid colorations obtained with such compounds as dimethyl-*p*-phenylenediamine and benzidine may be due to the peroxidic property of wood. The action of wood on a photographic plate in the dark has been attributed by Russell[1] to the liberation of hydrogen peroxide.

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[1] L. Zechmeister, "Zur Kenntnis der Cellulose und des Lignins," Diss. Zürich, (1913), p. 36.

[2] E. Crocker, *l.c.*

[3] A. Ihl, *Chem. Ztg.*, **13** (1889), 560; **15** (1891), 201.

[4] E. Nickel, *Chem. Ztg.* **17** (1893), 1243.

[5] G. Wocker, "Die Katalyse," **2** (1915), 567.

[6] C. F. Cross, E. J. Bevan and T. Heiberg, *J. Chem. Soc.*, **75** (1899), 752; *Ber.*, **40** (1907), 3120.

[7] P. Klason, *Ber.*, **53** (1920), 711; *cf.* E. C. Crocker, *l.c.*

In order to isolate the color-producing bodies, Wichelhaus and Lange[2] subjected coniferous wood to superheated steam at a temperature of 180°. Extraction of the distillate with ether yielded an oil, giving with lignin reagents, color reactions apparently identical with those obtained with wood. The distillate from 1200 grams of wood was separated into two fractions;[3] the first and largest fraction gave a green precipitate with phloroglucinol-hydrochloric acid, while the second gave a typical cherry-red precipitate. Paranitrophenylhydrazine gave a brick-red substance, $C_{18}H_{18}O_7N_6$, apparently a derivative of a keto-furfural formed from a hexose:

$$C_6H_{12}O_6 + O - H_2O = C_6H_8O_5 + H_2O.$$

According to a further paper,[4] two fractions were obtained boiling at 88 and at 95 to 105°, respectively, at 0.4-mm. pressure; from analyses the fractions were assigned the formulæ $C_{16}H_{22}O_9$ and $C_{16}H_{22}O_{10}$, and considered as compounds related to brasilin, $C_{16}H_{14}O_5$, and hæmatoxylin, $C_{16}H_{14}O_6$, which occur in dye woods. The color-producing constituents can be obtained by heating the wood with dry hydrogen chloride, removing the latter with an inert gas, and extracting with alcohol.[5]

Wood reacts but slowly with fuchsin-sulphurous acid solution. Ungar[6] obtained a yellowish-red coloration with spruce after 1 hour and an intense reddish violet after 18 hours.

It may be concluded that most of the so-called lignin reactions are due to bodies of an aldehydic nature, the structures of which are still problematical. The most reliable test for lignin is the purplish-red color of the chlorine-sodium sulphite reaction. The crude cellulose obtained by the cuprammonium extraction of wood, when treated with 72 per cent sulphuric acid to remove the carbohydrates, left a residue giving this characteristic color test for lignin.[7]

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[1] W. J. Russell, *Proc. Roy. Soc.*, **61** (1897), 424; **74** (1904), 131.

[2] H. Wichelhaus and M. Lange, *Ber.*, **49** (1916), 2001.

[3] H. Wichelhaus and M. Lange, *Ber.*, **50** (1917), 1683–1685.

[4] H. Wichelhaus, *Ber.*, **52** (1919), 2054–2056.

[5] H. Wichelhaus, *Chem. Ztg.*, **47** (1923), 865.

[6] E. Ungar, Diss. Budapest (1916), p. 48.

[7] A. W. Schorger, *J. Ind. Eng. Chem.*, **15** (1923), 812.

CHAPTER V

HEMICELLULOSES AND WOOD CELLULOSE

There is no unanimity of opinion regarding definitions for either a cellulose or a hemicellulose. In view of the several criterions available, a given carbohydrate might be placed in either class. Since it is impossible to discuss the hemicelluloses without taking wood cellulose into consideration, the two will be treated in sequence.

A hemicellulose may be broadly defined as a polysaccharide soluble in dilute alkalis and convertible into simple sugars by heating with dilute acids at atmospheric pressure. Until more data are available, the writer would add the further limitation that a hemicellulose, in the natural state, should be insoluble in boiling water. Unless this is done, the definition would include such totally dissimilar substances as starch that is soluble only in hot water; the galactan of western larch that is readily soluble in both cold and hot water; and the mannan of ivory nuts that is soluble in neither.

Wood gum after isolation with alkalis is soluble in hot water, but little xylan, araban, or mannan can be isolated from wood with boiling water alone. On the other hand, there is reason to believe that all the galactan, in coniferous wood, at least, can be completely extracted with water. Many of the hemicelluloses, once peptized with alkali, remain soluble in water, but there are exceptions. The mannan of ivory nuts, liberated from its copper compound with acid, is readily soluble in hot water, but on boiling the solution it separates in an insoluble form.[1] Other carbohydrates become insoluble in water by being completely dehydrated.

Carbohydrates such as starch, lichenin, and larch galactan should be placed in a distinct class, *hemisaccharides*.

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[1] J. L. Baker and T. H. Pope, *J. Chem. Soc.*, **77** (1900), 703.

The term "hemicellulose" was introduced by Schulze.[1] He defined as hemicelluloses those carbohydrates occurring in the plant cell that are dissolved by dilute alkalis, readily hydrolyzed by hot dilute mineral acids, and destroyed by F. Schulze's reagent. (Cellulose, comparatively speaking, is resistant to these reagents.) If cellulose were retained as a group name, it must be qualified; thus a gluco-cellulose would give only glucose on hydrolysis, while a manno-cellulose would give mannose in addition to glucose.

The hemicelluloses are anhydrides of hexose and pentose sugars. Xylan, araban, mannan, and galactan, as the names imply, give xylose, arabinose, mannose, and galactose, respectively, on hydrolysis. A hemicellulose giving both galactose and arabinose is a galacto-araban. Whether a compound of the latter type is a chemical individual or an intimate mixture of galactan and araban is not known.

It was realized by Schulze[2] that the action of hot dilute acids does not furnish a sharp distinction between a cellulose and a hemicellulose. Pelouze,[3] in 1859, pointed out that, contrary to the general opinion, a boiling dilute mineral acid acting on paper, linen, and sawdust produces some glucose.

The hemicelluloses were formerly known as reserve celluloses, the theory being that they were stored against a period of great metabolic activity, such as occurs in the germination of seeds[4] and the renewal of growth in woody plants in spring. It is true that in seeds some of the hemicelluloses, those occurring in the shell[5] excepted, are consumed in growth.[6] The pentosans in barley do not decrease during the malting process.[7] During the germination of seeds there may be an increase[8] or a decrease[9] of pentosans. Some investigators[8,9,10] believe that the pentosans do not serve as reserve materials, while others[1] hold that they may be consumed when the more readily utilizable carbohydrates are exhausted.

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[1] E. Schulze, *Ber.*, **24** (1891), 2285; *Z. physiol. Chem.*, **16** (1892), 391; **14** (1890), 227.

[2] E. Schulze, *Chem. Ztg.*, **19** (1894), 1465.

[3] J. Pelouze, *Compt. rend.*, **48** (1859), 327.

[4] R. Riess, *Landw. Jahrb.*, **18** (1889), 711.

[5] N. Castoro, *Z. physiol. Chem.*, **49** (1906), 107.

[6] E. Schulze and N. Castoro, *Z. physiol. Chem.*, **37** (1902), 40.

[7] B. Tollens and H. Glaubitz, *J. Landw.*, **45** (1897), 106.

[8] A. Schöne and B. Tollens, *J. Landw.*, **48** (1900), 349; C. F. Cross, E. J. Bevan, and C. Beadle, *Ber.*, **27** (1894), 1064.

[9] G. de Chalmot, *Am. Chem. J.*, **15** (1893), 276; **16** (1894), 589.

[10] K. Goetze and T. Pfeiffer, *Landw. Vers.-Sta.*, **47** (1896), 59.

The leaves of growing plants contain soluble pentoses. De Chalmot[2] found that in oak leaves the quantity of soluble pentoses is greater in the evening than in the morning. During the night they are converted into the insoluble form. Ravenna and Cereser[3] observed in the leaves of beans an increase in pentosans during the day. When carbohydrates were administered as food, dextrose especially produced a marked increase in pentosans, from which it was concluded that the simple sugars are the important factors in their formation.

During the growth of the corn plant there is a steady increase in pentosans. From a percentage of 7.4 in the kernel, it increases to 31.8 per cent in the cob at maturity. The free pentoses (as xylose) in the plant attained 1.66 per cent during the silk-forming stage.[4]

According to du Sablon,[5] hemicelluloses are formed in willow twigs in the fall and dissolved in spring. Storer[6] found that the gray birch (*Betula populifolia* Aiton) contained more pentosans in May than in October, but realized that the method of analysis rendered the results inconclusive. His results are too high. Schellenberg[7] examined twigs from various species of trees and could find no evidence of solution of the hemicelluloses, except possibly in the libriform fibers of *Robinia pseudacacia.*

The pentosans in the case of some plants at least are hydrophilic colloids. They are mucilagenous and have the power of swelling and taking up an enormous amount of water, properties possessed by the hexosans to a far more limited extent. Succulent plants possessing pentosans are able to take up and store large quantities of water that become available during dry periods.[1]

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[1] E. Schulze, *Z. physiol. Chem.*, **21** (1896), 392; K. Miyake, *J. Coll. Agr. Tôhoku Imp. Univ.*, **4** (1912), 327; C. Ravenna and O. Cereser, *Atti R. Acad. Lincei*, **18,** II (1909), 177; **19,** II (1910), 202; W. E. Tottingham *et al.*, *J. Biol. Chem.*, **15** (1921), 407.

[2] G. de Chalmot, *Am. Chem. J.*, **15** (1893), 21.

[3] C. Ravenna and O. Cereser, *l.c.*

[4] J. H. Ver Hulst, W. H. Peterson, and E. B. Fred, *J. Agr. Research*, **23** (1923), 655–663.

[5] L. du Sablon, *Rev. gén. botan.*, **16** (1904), 341.

[6] F. H. Storer, *Bull. Bussey Inst.*, **2** (1897), 387.

[7] H. C. Schellenberg, *Ber. botan. Ges.*, **23** (1905), 36.

Frank and Temme[2] thought that the wood gum in deciduous trees, like the resin in conifers, had a pathological significance and served to protect the wood beneath a wound from atmospheric influences. This might be the case with a true gum such as is secreted by *Prunus*, but not with "wood gum."

If pentosans have a special function[3] in nature, no theory of general applicability has yet been advanced. They appear to be structural and not reserve materials in wood where they serve as a cement to hold the fibers together.

De Chalmot[4] could find no relation between the pentosan content and the hardness, toughness, and other properties of the wood. While pentosans may play some part in the formation of wood, large amounts are not essential, as shown in the case of hemlock (*Tsuga canadensis*), which contains but 6 per cent. There was variability in the amount of pentosans between trees of the same species and between specimens of wood of the same age taken from different portions of the same tree. Age was of slight influence; the immature wood of *Pinus tæda*, however, contained 7.65 per cent of pentosans in comparison with 9.85 per cent for the mature wood.[5]

Tollens[6] thought that pentosans were formed by atmospheric oxidation of starch or cellulose with the aid of ferments. A similar suggestion was made by de Chalmot.[7] Pentoses are formed from hexoses by oxidation of the terminal primary alcohol group and the splitting out of carbon dioxide from the corresponding acid. The aldehyde groups are condensed so as to be protected from oxidation, so that pentosans result. Glucuronic acid was suggested as an intermediate product.

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[1] H. A. Spoehr, "The Carbohydrate Economy of Cacti," *Carnegie Inst. Pub.*, **287**, 79. Washington.

[2] B. Frank and F. Temme, *Biedermann's Centr.*, **14** (1885), 285–286.

[3] Science advances by conservative speculation, but teleological deductions, owing to their intriguing nature, should be accepted with caution. St. Pierre was so impressed by the economy of nature that in his eyes melons were ribbed that they might be carved and eaten more readily. At the opposite extreme lies Bacon's dictum, "*Causarum finalium inquisito sterilis est, et tanquam virgo Deo consecrata, nihil parit.*"

[4] G. de Chalmot, *Am. Chem. J.*, **16** (1894), 218.

[5] G. de Chalmot, *Am. Chem. J.*, **16** (1894), 611.

[6] B. Tollens, *J. Landw.*, **44** (1896), 187.

[7] G. de Chalmot, *Am. Chem. J.*, **16** (1893), 610.

Spoehr[1] has actually isolated 0.1 per cent of the lactone of glucuronic acid from cactus gum. He believes that under the influence of sunlight glucuronic acid breaks up into carbon dioxide and *l*-xylose. It is an old observation that *d*-glucose and *l*-xylose are associated in nature, but if the pentoses were formed by oxidation of the hexoses, *d*-glucose, according to Spoehr, would give *d*-arabinose. This is correct if oxidation is assumed to take place at the aldehyde group, but *l*-xylose would be formed if oxidation took place at the primary alcohol group.

The hemicelluloses, just as cotton cellulose, are soluble in cuprammonium solution.[2] In the natural state their solubility may be very slight; however, treatment with very dilute, boiling hydrochloric acid for 5 minutes, or cold 10 per cent acid for 24 hours, renders them completely soluble in cuprammonium solution.[3]

When birch wood (*Betula lutea*) was ground in a ball mill with cuprammonium solution, the pentosans were dissolved more rapidly than the cellulose, though their removal was by no means complete.[4]

Wood gum dissolved in cuprammonium solution differs from cellulose in the same solvent in that it is not precipitated by acids until alcohol is added.[5] In case of a mixture the cellulose would be expected to carry down a large portion of the wood gum. According to Salkowski,[6] both xylan and cellulose are precipitated from their cuprammonium solutions by sodium hydroxide and cannot be separated in this way.

The hemicelluloses are completely soluble in dilute caustic alkalis.[7] A cold or hot 5 per cent solution of sodium hydroxide is usually employed for their extraction. Isolated hemicelluloses are also soluble in a hot, saturated solution of sodium carbonate.[1] Wood gum may be isolated with lime water but not so conveniently as with the caustic alkalis.[2]

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[1] H. A. Spoehr, *l.c.*, 42, 75.

[2] R. Riess, *Landw. Jahrb.*, **18** (1889), 747; E. Schulze *et al.*, *Z. physiol. Chem.*, **14** (1890), 245, 266; *Ber.*, **22** (1889), 1194.

[3] E. Schulze, *Z. physiol. Chem.*, **16** (1892), 410.

[4] A. W. Schorger, *J. Ind. Eng. Chem.*, **16** (1924), 144.

[5] F. Koch, *Pharm. Z. Russl.*, **25** (1886), 657.

[6] E. Salkowski, *Z. physiol. Chem.*, **34** (1901), 180.

[7] E. Schulze, *Z. physiol. Chem.*, **16** (1892), 409.

According to Hoffmeister,[3] pentosans are not always readily dissolved by caustic soda, while hexosans are frequently readily so. A 5 per cent solution of caustic soda extracted xylan very slowly from beech-wood cellulose; a 10 per cent solution removed it incompletely, the residual cellulose giving 1.98 per cent of furfural.[4]

Pine wood felled in spring was extracted with ether. Alternate extraction with water, or 0.3 per cent acetic acid, and alcohol gave 13.9 per cent of extract.[5] Wood felled in winter gave only one-seventh as much extract. The yield of furfural from the extract showed about 23 per cent of xylose.

Pentosans were removed slowly and incompletely when aspen wood was ground in a ball mill with dilute sodium hydroxide for three periods of 48, 24, and 18 hours, respectively.[6] The amount of pentosans removed depends on the strength of the alkalis, though not proportionally, as shown by the following table:

Strength of NaOH solution, per cent	Extraction No.	Wood dissolved, per cent	Pentosan in residue	
			Per cent	Per cent of total pentosans
5	1	31.29	8.62	25.82
	2	3.38	6.82	19.42
	3	1.68	6.71	18.62
2	1	27.82	11.58	36.44
	2	2.52	9.67	29.37
	3	1.71	9.23	27.34
1	1	24.64	16.01	52.60
	2	3.57	13.58	42.50
	3	1.69	12.48	38.14

[1] M. H. O'Dwyer, *Biochem. J.*, **17** (1893), 50.

[2] E. R. Flint and B. Tollens, *Landw. Vers.-Sta.*, **42** (1893), 404.

[3] W. Hoffmeister, *Landw. Vers.-Sta.*, **50** (1898), 360.

[4] M. H. O'Dwyer, *Biochem. J.*, **17** (1923), 501–509.

[5] S. Schmidt-Nielsen, *Chem. Zeit. Rep.*, **45** (1921), 32.

[5] A. W. Schorger, *J. Ind. Eng. Chem.*, **16** (1924), 142.

It should be noted that sodium hydroxide as dilute as 1 per cent removed 61.86 per cent of the total pentosans.

The amount of xylan remaining in straw cellulose isolated by chlorination and extraction with alkali at 70° depends upon the strength of the alkali used.[1] With a 1 per cent solution of sodium hydroxide, the cellulose gave 13.3 per cent furfural, and with a 3 per cent solution, 9.3 per cent furfural. Until the lignin is removed from the straw, alkali will not extract all the xylan, indicating a close association between pentosans and lignin.

Schwalbe[2] removes the pentosans from wood pulp by heating it with magnesium sulphite in the presence of calcium or magnesium oxide.

Extraction with alkalis alters the hemicelluloses.[3] The xylan remaining in beech wood, after removal of the lignin, was not affected by chlorine dioxide; it was attacked, however, after isolation with 5 per cent sodium hydroxide.[4] The same was true of the mannan of ivory nuts.

The xylan in straw is very slightly attacked by chlorine.[5] Xylan, isolated with alkali, after being in contact with chlorine for 15 hours retained 16.8 per cent of chlorine as xylan chloride, while an equivalent amount of hydrogen chloride was formed. This indicates that chlorine attacks xylan by substitution. According to Briggs,[6] the presence of chlorine is due more probably to the contamination of the xylan with lignin. In the case of esparto, at least, alkali simultaneously extracts a portion of the lignin, and this is separable from xylan only by boiling the extract.

Xylan or wood gum, once isolated, is partially or completely soluble in boiling water.[7] Hemicelluloses may be isolated from wood by heating it with water[8] under a pressure corresponding to a temperature of 180°. They are also soluble in glycerine[1] at a temperature of 210°.

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[1] E. Heuser and A. Haug, *Z. angew. Chem.*, **31** (1918), 166.

[2] C. G. Schwalbe, G. P. 378260 (1921).

[3] J. S. Alexandrowicz, *Arch. Physiol.*, **150** (1913), 80.

[4] E. Schmidt and E. Graumann, *Ber.*, **54** (1921), 1867.

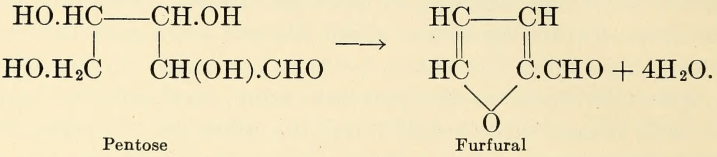
[5] E. Heuser and A. Haug, *Z. angew. Chem.*, **31** (1918), 104.

[6] J. F. Briggs, *Ann. Rep. Soc. Chem. Ind.*, **3** (1918), 128.

[7] E. Salkowski, *Z. physiol. Chem.*, **117** (1921), 48; M. H. O'Dwyer, *l.c.*, 501.

[8] K. Fromherz, *Z. physiol. Chem.*, **50** (1906), 209; W. Koch, Diss. Freiburg (1909).

Characteristic of the pentoses and their polyanhydrides is the formation of furfural by dehydration when heated with dilute mineral acids. Stenhouse[2] appears to have been the first to prepare furfural by distilling with a mineral acid, in this case sulphuric acid, and to show that it may be procured from most vegetable materials. The highest yields of furfural were obtained from the hardwoods.[3]



Furfural may be produced by heating pentosans with water under pressure. Corncobs[4] give 20 per cent of furfural by distillation with hydrochloric acid, while with steam the maximum yield is about 10 per cent. The optimum conditions are a reaction period of 2 hours at 180°, and a ratio of cobs to water of not more than 1:4.

A large number[5] of determinations of the pentosans in woods has been made by means of the furfural reaction. De Chalmot[6] examined the following American species:

Species	Pentosans,[1] Per Cent
Tulip tree (*Liriodendron tulipifera* Linn.)	19.1
Cucumber tree (*Magnolia acuminata* Linn.)	17.7
Wild red cherry (*Prunus pennsylvanica* Linn.)	19.7
Redbud (*Cercis canadensis* Linn.)	21.1
Silver maple (*Acer dasycarpum* Ehr.)	22.1
Red gum (*Liquidambar styraciflua* Linn.)	21.1
American holly (*Ilex opaca* Ait.)	24.6
Dogwood (*Cornus florida* Linn.)	21.6

[1] Not corrected for so-called "methylpentosans." For more recent data see Table 2' p. 34.

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[1] M. Hönig, *Chem. Ztg.*, **14** (1890), 902.

[2] J. Stenhouse, *Phil. Mag.*, [3] **18** (1841), 122–124.

[3] J. Stenhouse, *Phil. Mag.*, [3] **37** (1850), 227.

[4] F. B. La Forge, *J. Ind. Eng. Chem.*, **15** (1923), 499.

[5] B. Tollens, *J. Landw.*, **44** (1896), 171; *Z. angew. Chem.*, **15** (1902), 508.

[6] G. de Chalmot, *Am. Chem. J.*, **16** (1894), 218.

Species	Pentosans, Per Cent
Black gum (*Nyssa sylvatica* Marsh.)	20.8
White ash (*Fraxinus americana* Linn.)	17.5
Water ash (*Fraxinus platycarpa* Michx.)	17.4
Butternut (*Juglans cinerea* Linn.)	19.2
Shagbark hickory (*Carya alba* Nutt.)	21.2
Willow (*Salix sp.*)	21.0
Birch (*Betula sp.*)	23.4
Beech (*Fagus ferruginea* Ait.)	21.0
Willow oak (*Quercus phellos* Linn.)	21.6
White oak (*Quercus alba* Linn.)	20.4
Red oak (*Quercus rubra* Linn.)	21.7
Water oak (*Quercus nigra* Linn.)	21.3
White elm (*Ulmus americana* Linn.)	17.4
Sycamore (*Platanus occidentalis* Linn.)	21.6
Red juniper (*Juniperus virginiana* Linn.)	10.4
White pine (*Pinus strobus* Linn.)	7.5
Shortleaf pine (*Pinus mitis* Michx.)	8.8
Hemlock (*Tsuga canadensis* Carr.)	6.0

The pentosans are low, 6 to 10 per cent, in the gymnosperms, while uniformly high, 17 to 25 per cent, in the dicotyledons.

Furfuroids.—It is frequently difficult to establish definitely the presence of pentosans in plant substances, even though they give furfural on distillation with 12 per cent hydrochloric acid; furthermore, the oxycelluloses, particularly those formed by oxidation with chromic acid, give appreciable quantities of furfural. For these reasons, Cross and Bevan,[1] in 1893, advanced the hypothesis that oxycelluloses or "furfuroids" exist in nature. Esparto and the cereal straw celluloses, *e.g.*, were classed as oxycelluloses.[2] They have tenaciously defended their position.[3]

Some support was given to this view by Tollens,[4] owing to the fact that some substances gave furfural but only a faint pentose reaction,[5] *i.e.*, a pink color on warming with phloroglucinol and hydrochloric acid. De Chalmot[1] and Stone,[2] on the other hand, considered all the furfural yielded by natural substances to be derived from pentosans.

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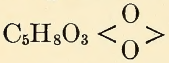
[1] C. F. Cross, E. J. Bevan, and C. Beadle, *Ber.*, **26** (1893), 2520; **27** (1894), 1061, 1456.

[2] C. Smith, *Proc. Chem. Soc.*, **10** (1894), 89.

[3] C. F. Cross, E. J. Bevan, and C. Beadle, *J. Am. Chem. Soc.*, **17** (1895), 286; C. F. Cross, *Chem. News*, **71** (1895), 68; C. F. Cross and E. J. Bevan *J. Chem. Soc.*, **113** (1918), 182.

[4] B. Tollens, *Ann.*, **286** (1895), 301; H. Suringar and B. Tollens, *Z. angew. Chem.*, **9** (1896), 746.

[5] B. Tollens, *Ber.*, **29** (1896), 1202.

In 1896, Cross and Bevan[3] investigated the furfural-yielding complex in the cereal straws. This could be split off by dissolving the cellulose in sulphuric acid of sp. gr. 1.55 to 1.65; on the addition of water the cellulose was precipitated, while the furfuroids remained in solution. The furfuroids gave no pentose reaction but yielded 38 to 42 per cent of furfural. They assigned to furfuroids the formula of a pentose monoformal,  $C_5H_8O_3 < \begin{matrix} O \\ O \end{matrix} > CH_2$, that theoretically would give 44 per cent of furfural.

According to Heuser[4] there is no relation between the yield of furfural and the amount of oxycelluose present, as indicated by the copper number. A straw cellulose having a copper number of 8.60 gave 2.09 per cent furfural; the latter value was not changed on increasing the copper number to 15.5 by further bleaching. The failure of Cross and Bevan to identify pentoses in straw cellulose is attributed to faulty experiment. The phloroglucinol reaction is significant only in the case of aqueous solutions of pure pentoses, and even then great care must be exercised; if furfural is produced, the green color masks the rose.

Kunz[5] states that barley chaff contains two forms of substances yielding furfural, the one being easily hydrolyzed, the other with difficulty; both, however, appear to be true pentosans. There is no foundation, in fact, for the pentose monoformal formula.

In 1918, Cross and Bevan[6] returned to the subject of furfuroids. Their experimental data point directly to the presence of a large proportion of pentosans in esparto cellulose, though some support is found for the presence of a small amount of furfuroids. Esparto cellulose, isolated by cooking raw esparto at 130° with 17 per cent of sodium hydroxide in 3 to 4 per cent solution, gave 12.5

[1] G. de Chalmot, *Ber.*, **27** (1894), 1489; *Am. Chem. J.*, **15** (1893), 21.

[2] W. E. Stone, *Chem. News.*, **71** (1895), 40.

[3] C. F. Cross, E. J. Bevan, and C. Smith, *J. Chem. Soc.*, **69** (1896), 804; **71** (1897), 1001; *Ber.*, **29** (1896), 1457; *J. Am. Chem. Soc.*, **18** (1896), 8.

[4] E. Heuser and A. Haug, *Z. angew. Chem.*, **31** (1918), 172.

[5] E. Kunz, *Biochem, Z.*, **74** (1916), 312–339.

[6] C. F. Cross and E. J. Bevan, *J. Chem. Soc.*, **113** (1918), 182–187.

per cent of furfural. From the cooking liquor was isolated a practically pure pentosan, since it gave 50 per cent of furfural. Treatment of the cellulose with alkali and acid produced selective solution of the pentosans, but there was always a loss of furfural. The distribution of furfural in the α-, β-, and γ-celluloses, determined with 17.5 per cent sodium hydroxide, was:

	Yield, per cent	Furfural, per cent
α-Cellulose	84.14	3.36
β-Cellulose		
γ-Cellulose	15.86	4.12
Total	.....	7.48

Since the original cellulose contained 12.5 per cent furfural, there was a loss of 5 per cent by the alkaline treatment. It has been satisfactorily shown, however, that the furfural obtainable from esparto cellulose comes mainly from a pentosan yielding xylose on hydrolysis.[1]

When sulphite wood pulp is dissolved in strong hydrochloric acid, 20 per cent of the apparent pentosans are destroyed.[2] The possibility that the substances destroyed are not true pentosans is indicated by the fact that the pulp, after extraction with 17 per cent sodium hydroxide, contains 3 per cent of pentosans and these are not destroyed when the extracted pulp is dissolved in the acid. Furthermore, the pentosans in the hemicellulose precipitated from the alkaline extract with alcohol can be quantitatively accounted for after solution in hydrochloric acid; hence the apparent pentosans are destroyed by the acid and are not precipitable from the alkaline solution with alcohol.

Tottingham and Gerhardt[3] hydrolyzed the spur tissue of the apple tree with dilute sulphuric acid and found that most of the constituents yielding furfural were destroyed by fermentation with a Carlsberg yeast; thus they were not true pentosans.

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[1] J. C. Irvine and E. L. Hirst, *J. Chem. Soc.*, **125** (1924), 15.

[2] E. Hägglund and F. W. Klingstedt, *Cellulosechemie*, **5** (1924), 57.

[3] W. E. Tottingham and F. Gerhardt, *J. Ind. Eng. Chem.*, **16** (1924), 139.

The hydrolysate with 4 per cent sulphuric acid showed 11.9 per cent of pentoses before fermentation and only 2.9 per cent of pentoses afterwards.

Methylpentosans.—No adequate proof exists that methylpentosans occur in wood, methylfurfural or a methylpentose having never been satisfactorily identified.[1] The reports of their presence in numerous species of woods are due to failure to employ precise methods of examination. Most of the determinations are based on the observation of Votocek[2] that the phloroglucide of methylfurfural is soluble in alcohol. It is most probable that the soluble phloroglucide is that of ω-hydroxymethylfurfural. This aldehyde[3] is always formed in small amount during the distillation of hexose carbohydrates with acids. Beech wood gave 0.50 per cent of ω-hydroxymethylfurfural. Most of the aldehyde is formed at the end of the acid distillation. Methylfurfural and ω-hydroxymethylfurfural, unlike furfural, do not color aniline acetate paper, but give a pink color with an alcoholic solution of aniline.

Other substances of unknown origin increase the solubility of the phloroglucide precipitate. Fraps[4] found that the acid furfural distillate from plant materials lost from 7 to 23 per cent on redistillation. The substances destroyed were called "furaloids." A portion of the loss is without doubt due to ω-hydroxymethylfurfural, as this aldehyde breaks down to formic and lævulinic acids.

The spectroscopic detection of methylfurfural by the method of Tollens,[5] who reported the presence of methylpentosan in pine wood, must be used with care. A hydrochloric acid solution of methylfurfural phloroglucide gives absorption bands between the F and G lines near F, and hydroxymethylfurfural, absorption bands between the E and F lines near F.[6] Owing to the similarity of the absorption bands, it is necessary, when both aldehydes are present, to destroy the ω-hydroxymethylfurfural by redistillation in the presence of hydrochloric acid.[1]

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[1] A. W. Schorger, *J. Ind. Eng. Chem.*, **9** (1917), 562; **16** (1924), 143.

[2] E. Votocek, *Ber.*, **30** (1897), 1195.

[3] M. Cunningham and C. Dorée, *Biochem. J.*, **8** (1914), 438.

[4] G. S. Fraps, *Am. Chem. J.*, **25** (1901), 501.

[5] J. A. Widtsoe and B. Tollens, *Ber.*, **33** (1900), 143; K. Oshima and B. Tollens, *Ibid.*, **34** (1901), 1425.

[6] K. Oshima and T. Tadokoro, *J. Chem. Soc. Japan*, **39** (1918), 23.

Leaves of *Betula, Fraxinus, Acer, Sorbus, Tilia,* and *Pinus* gave only a weak methylpentosan reaction as determined by the absorbtion spectra.[2] Schirmer[3] reports 12.18 per cent pentosan and 10.26 per cent methylpentosan in the mucilage obtained from the bark of the slippery elm (*Ulmus fulva*).

The apparent methylpentosan content of wood may attain 4.5 per cent.[4] Sebelien[5] obtained 4.70 per cent for spruce.

Preparation of Hemicelluloses.—Before attempting the isolation of hemicelluloses, it is advisable to digest the mother substance, particularly if it is wood, with a 2 per cent solution of ammonia in the cold for one or more periods of 24 hours each. After removal of the ammoniacal liquor, the residue is thoroughly washed with water. In this way most of the tannins, resins, and coloring matter are removed.

Wheeler and Tollens[6] prepared wood gum from beech by digesting the purified sawdust with 5 per cent sodium hydroxide solution at room temperature for 48 hours, and adding an equal volume of 95 per cent alcohol to the filtrate to precipitate the sodium compound of the gum. The precipitate immersed in alcohol was decomposed with hydrochloric acid and the gum washed with alcohol and ether. The method does not give a pure product.

The most satisfactory method from the standpoint of purity is based on the observation of Salkowski[7] that most of the hemicelluloses are precipitated from their alkaline solution by Fehling's solution. According to Browne,[8] the Salkowski method of purification is attended with great loss of hemicellulose in the case of sugar-cane fiber. This is evidently due to the fact that certain forms of araban, such as those from beets and cherry gum, are not precipitated.[1] Advantage might be taken of this property to separate some of the hemicelluloses from mixtures.

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[1] K. Oshima and K. Kondo, *J. Chem. Soc. Japan,* **39** (1918), 185.

[2] P. R. Solleid, *Chem. Ztg.,* **25** (1901), 1138.

[3] W. Schirmer, *Arch. Pharm.,* **250** (1912), 249.

[4] A. W. Schorger, *J. Ind. Eng. Chem.,* **9** (1917), 556.

[5] J. Sebelien, *Chem. Ztg.,* **30** (1906), 401.

[6] H. Wheeler and B. Tollens, *Ann.,* **254** (1889), 304.

[7] E. Salkowski, *Ber.,* **27** (1894), 497.

[8] C. A. Browne, *J. Am. Chem. Soc.,* **26** (1904), 1229.

O'Dwyer[2] extracted the hemicellulose from white oak with cold 4 per cent sodium hydroxide and precipitated it as the sodium compound with alcohol. The hemicellulose, set free with acetic acid, was purified by the method used by Baker and Pope[3] for isolating mannogalactan from the clearing nut (*Strychnos potatorum*) and mannan from the ivory nut. The ground nuts are extracted with a 2 per cent solution of caustic soda for 2 hours in a water bath, filtered through glass wool, and an excess of Fehling's solution added to the filtrate. The blue precipitate settles to a pasty mass. Excess of copper salt and other impurities are removed by kneading and washing with water. The water must be slightly alkaline, as the precipitate becomes soluble in pure water. Cold dilute hydrochloric or acetic acid is added to decompose the copper compound, the light-green solution thus obtained being filtered and poured into strong alcohol. The white precipitate is washed with cold and then with hot alcohol, again dissolved in water, and reprecipitated with alcohol. The product is collected, dried in the air, then at 105°, and cooled in a vacuum.

Salkowski[4] prepared xylan from wheat straw as follows: boil 100 grams of comminuted straw with 2.5 liters of 6 per cent caustic soda for 45 minutes. After cooling, filter through linen, press the residue, and allow the filtrate to stand in a tall cylinder for several days to settle. The supernatant liquid is decanted, mixed with a liter of Fehling's solution, and gently heated to flocculate the precipitate. The precipitate is filtered on linen, washed once with water, and triturated with hydrochloric acid, of a concentration of about 12 per cent, until blue particles are no longer visible. The pulpy mass is mixed with 2 to 3 volumes of 93 per cent alcohol, filtered, washed first with 50 per cent alcohol, then with strong alcohol; now let stand several days with absolute alcohol. The xylan is finally triturated with ether and the ether removed by gentle heat.

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[1] E. Salkowski, *Z. physiol. Chem.*, **34** (1901), 171.

[2] M. H. O'Dwyer, *l.c.*, 502.

[3] J. L. Baker and T. H. Pope, *J. Chem. Soc.*, **77** (1900), 699.

[4] E. Salkowski, *Z. physiol. Chem.*, **34** (1901), 163.

A xylan free from nitrogen, araban, mannan, and galactan, but containing 1.25 to 2.25 per cent of ash, is obtained in a yield of 22 to 23 per cent. For further purification, the xylan can be redissolved in caustic soda and the precipitation with Fehling's solution repeated. A cuprammonium solution may be used, but the precipitate is more gelatinous and difficult to handle.

A purer product is obtained[1] by diluting the alkaline filtrate to 14 liters and allowing to settle for several days. The solution is filtered, evaporated to the original volume, and again filtered through asbestos. The precipitate with Fehling's solution is dissolved by heating with ammonium hydroxide and the solution filtered. The filtrate is strongly acidified with hydrochloric acid and 1.5 volumes of 95 per cent alcohol added to complete the precipitation of the xylan.

Heuser[2] starts with bleached straw pulp and obtains a xylan with only 0.35 per cent ash by a modification of Salkowski's method. The blue precipitate is kneaded twice with 80 per cent alcohol and filtered. The residue is then triturated with 95 per cent alcohol until all lumps disappear. Hydrogen chloride is then passed into the alcoholic suspension until the precipitate is pure white, a procedure requiring 3 to 4 hours. The precipitate is filtered off, washed repeatedly with 30 per cent alcohol, finally with ether, and dried. The xylan is obtained as a loose, white, odorless powder of a purity of 96 per cent. The yield is 19 per cent.

A less pure xylan (93.8 per cent) is obtained by mixing the caustic soda solution with an equal volume of 96 per cent alcohol and passing in hydrogen chloride.[3]

Hydrolysis of Hemicelluloses.—While wood gum yields mainly xylose on hydrolysis, other sugars, including hexoses, are also obtained. O'Dwyer[4] obtained 51.5 per cent xylose, 18.5 per cent arabinose, and 30 per cent of a mixture of galactose and mannose from the hemicellulose of white oak. This partially explains the low pentosan content of wood gum. Flint and Tollens[1] obtained the following:

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[1] E. Salkowski, *Z. physiol. Chem.*, **117** (1921), 48.

[2] E. Heuser and M. Braden, *J. prakt. Chem.*, **103** (1921), 69.

[3] E. Heuser and M. Braden, *J. prakt. Chem.*, **104** (1922), 259.

[4] M. H. O'Dwyer, *l.c.*, 503.

	Wood gum No.			
	1	2	3	4
Pentosan, per cent	65.36	79.05	81.02	56.08

Pentosans are hydrolyzed more rapidly by hydrochloric acid than sulphuric acid.[2] Councler[3] boiled 15.5 grams of beechwood gum with 200 cubic centimeters of water and 10 cubic centimeters of hydrochloric acid of sp. gr. 1.19 for 2.5 to 3 hours, and obtained 9.63 grams of pure xylose. Saccharification is accompanied by the formation of humus and dextrin-like bodies.

High yields of xylose from xylan are difficult to obtain, owing to the partial conversion of xylose to furfural; for this reason sulphuric acid is preferable to hydrochloric.[4] A 67 per cent yield of xylose was obtained by boiling 10 grams of xylan in 400 cubic centimeters of 5 per cent sulphuric acid for 70 minutes; and a 50.6 per cent yield by hydrolysis with 5 per cent hydrochloric acid for 30 minutes. The highest yield of xylose (84 per cent) and absence of furfural formation is attained by heating xylan with 45 parts of 3 per cent nitric acid for 1 hour.[5] The xylan goes completely into solution after heating at 100° for 1 to 2 minutes. Evidently, dextrins are formed, since reduction indicates 58.72 per cent of xylose and no sugar can be isolated.

The decomposition of the pentose sugars during the hydrolysis of pentosans is much greater than when the pure sugars are heated with acids.[6] Xylose is less stable than arabinose. After heating 2 grams of sugar in 50 cubic centimeters of 10 per cent sulphuric acid, on a boiling water bath for 12 hours, there remained:

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[1] E. R. Flint and B. Tollens, *Ber.*, **25** (1892), 2912; *Landw. Vers.-Sta.*, **42** (1893), 381; cf. E. Kröber, *J. Landw.*, **49** (1901), 9.

[2] R. Hauers and B. Tollens, *Ber.*, **36** (1903), 3306.

[3] C. Councler, *Chem. Ztg.*, **16** (1892), 1719.

[4] E. Heuser and L. Brunner, *J. prakt. Chem.*, **104** (1922), 264–281; E. Heuser and E. Kürschner, *Ibid.*, **103** (1921), 75–102.

[5] E. Heuser and G. Jayme, *J. prakt. Chem.*, **105** (1923), 232–241.

[6] E. Schulze and B. Tollens, *Landw. Vers.-Sta.*, **40** (1892), 379.

	Humus, per cent	Residual sugar, per cent
Arabinose	3.27	84.54
Xylose	6.62	73.80

Wood Gum. Xylan.—"Wood gum" is not a true gum, since in the natural state it does not swell and dissolve in water. It consists mainly of xylan, usually with small amounts of mannan, araban, and galactan.

Poumarède and Figuier,[1] by the extraction of wood with alkali, obtained a substance having the properties of pectin. It was looked upon as identical with arabinic acid.[2] In 1879 Thomsen[3] investigated the extractive and called it wood gum. A large amount of gum was obtainable from birch wood by extracting it with cold caustic soda, sp. gr. 1.1 to 1.19, and precipitating with acid; pine gave very little gum. Sawdust from birch heartwood, after purification by extraction with water, alcohol, ether, alcohol, water, ammonia, and water, gave 19.7 per cent of wood gum.

Koch[4] also found that wood gum occurred abundantly in the broad-leaved trees, but sparingly in the gymnosperms. He found that alcohol added to the alkaline extract precipitated a compound containing sodium, "$5C_6H_{10}O_5:NaOH$." Hydrolysis gave an unknown, easily crystallizable sugar that he called "wood sugar." It had the following properties: m.p. 145°; specific rotation $[\alpha]_D = +23.41°$; unfermentable; and formed with phenylhydrazine long yellow needles, m.p. 160°.

It remained for Tollens[5] and his associates to clarify the composition of wood gum. By one extraction with sodium hydroxide, 1300 grams of birch sawdust gave from 63 to 70 grams of nearly white wood gum. A second extraction gave 14 grams of a dark product. The purified gum dissolved completely in sodium hydroxide of a concentration slightly over 2 per cent.[1] Ultimate analysis agreed with the formula $C_6H_{10}O_5$; however, hydrolysis yielded the second known pentose sugar, xylose, having $[\alpha]_D = +18$ to 19°. From 60 grams of gum, 16 grams of crystalline sugar were obtained.

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[1] J. A. Poumarède and L. Figuier, *Compt. rend.*, **23** (1846), 918.

[2] E. Reichardt, *Arch. Pharm.*, **7** (1877), 116.

[3] T. Thomsen, *J. prakt. Chem.*, **127** (1879), 146–168.

[4] F. Koch, *Pharm. Z. Russl.*, **25** (1886), 619–770.

[5] H. Wheeler and B. Tollens, *Ann.*, **254** (1889), 304–320; *Ber.*, **22** (1889), 1046.

Fir wood yielded 4.0 per cent of wood gum.[2] Hydrolysis gave xylose having $[\alpha]_D = +18.69°$, and yielding an osazone of m.p. 157.5 to 158.5°.

Okumura[3] determined the wood gum in various species of Japanese woods by extraction with 5 per cent sodium hydroxide. The yields varied from 0.961 (*Abies firma*) to 19.72 per cent (*Fagus sieboldi*).

It is of interest that, while the true gum[4] secreted from the bark of the cherry yields arabinose with a little xylose, the "gum" of the wood gives mainly xylose.[5]

Wood gum dissolved in dilute sodium hydroxide is strongly *l*-rotatory.

Source	$[\alpha]_D$	Author
Birch..............	−92.73 to −96.55°	Koch, *l.c.*
Beech.............	−69.62	Wheeler and Tollens, *l.c.*
	−81.0 to −83.6	Thomsen, *Ber.*, **14** (1881), 136
	−84.0	Thomsen, *Ber.*, **13** (1880), 2168
White oak.........	−75	O'Dwyer, *l.c.*

Wood gum is highly hygroscopic and is usually high in ash. Two samples examined by Councler[6] had the following composition:

Source	Ash, per cent	Water, per cent	Organic matter, per cent
Beech wood..........................	1.79	17.44	80.77
Straw paper..........................	1.23	13.36	85.41

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[1] H. Wheeler and B. Tollens, *Ann.*, **254** (1889), 320.

[2] H. Wheeler and B. Tollens, *Ann.*, **254** (1889), 323.

[3] J. Okumura, *Bull. Coll. Agr. Japan*, **2** (1894), 76.

[4] C. A. Browne and B. Tollens, *Ber.*, **35** (1902), 1466.

[5] E. W. Allen and B. Tollens, *Ann.*, **260** (1890), 296.

[6] C. Councler, *Chem. Ztg.*, **16** (1892), 1719.

Xylan from corncobs contained 13.5 per cent hygroscopic moisture and that from white birch (*Betula alba*) 9.42 to 10.26 per cent.[1] Koch[2] heated wood gum at 110° and obtained the following values:

Source	Hygroscopic Water, Per Cent
Quebracho wood	15.34
Oak wood	16.95
Walnut shells	19.93

Wood gum is colored by the phloroglucinol reagent only on warming, while lignin is colored in the cold.[3]

Pure beech-wood gum has been stated[4] to reduce a mercuric chloride solution on standing 4 weeks. Five grams of gum reduced 2.8 grams of mercuric chloride in a solution of 10 grams of the salt in 285 cubic centimeters of water. The purity of the gum is open to question.

Pure xylan should have the formula $C_5H_8O_4$. Judging from ultimate analyses,[5] the pure compound has seldom been obtained. Aside from non-carbohydrates, the pentosans are usually contaminated with hexosans. A wood gum prepared from beech by the method of Wheeler and Tollens contained 2.8 per cent methoxyl, the original wood 5.4 per cent.[6] Pure xylan, free from lignin, does not give the methoxyl reaction.[7]

König[8] obtained succinic acid, m.p. 185°, by fusing beech-wood gum with caustic potash. Catechol was not formed. Straw xylan[9] fused with 10 parts of caustic potash at 230 to 280° gave about 50 per cent of oxalic acid, 13 to 15 per cent of acetic acid, and 8 to 12 per cent of formic acid. A slight amount of succinic acid could be detected. The catechol and protocatechuic acid, qualitatively detected, were probably formed from ligneous impurities.

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[1] S. W. Johnson, *J. Am. Chem. Soc.*, **18** (1896), 214.

[2] F. Koch, *Pharm. Z. Russl.*, **25** (1886), 655.

[3] H. Wheeler and B. Tollens, *Ann.*, **254** (1889), 332.

[4] A. Link and A. Voswinkel, *Pharm. Zentralhalle*, **31** (1890), 679.

[5] S. W. Johnson, *l.c.*; F. Koch, *l.c.*, 670; H. Wheeler and B. Tollens, *l.c.*, 321; M. H. O'Dwyer, *l.c.*, 503.

[6] R. Benedict and M. Bamberger, *Monatsh.*, **11** (1890), 262.

[7] E. Heuser and M. Braden, *J. prakt. Chem.*, **104** (1922), 259.

[8] F. König, *Cellulosechemie*, **2** (1921), 118.

[9] E. Heuser and J. Roth, *J. prakt. Chem.*, **107** (1924), 1–6.

When xylan is dissolved in 2.5 times its weight of nitric acid (sp. gr. 1.2) at 70°, and the solution held at 45°, 21.7 per cent of the theoretical yield of trihydroxyglutaric acid is formed.[1] With twice the weight of nitric acid the chief product is oxalic acid.

Birch-wood gum heated with water at 84 pounds steam pressure for 2 hours gave 0.13 to 0.16 per cent of acetic acid and 0.11 to 0.16 per cent formic acid.[2]

Birch-wood gum on destructive distillation[2] gave the following:

	Per Cent
Charcoal	37.2
Tar and oil	33.6
Pyroligneous acid	33.6
Gas	18.1

The pyroligneous acid contained 9.0 per cent of furfural. The yields of acetic and formic acids were 0.29 and 0.17 per cent, respectively, so that wood gum is of no importance in the formation of acetic acid in the destructive distillation of wood. The wood gum from fir gave similar results.

Heuser and Scherer[3] distilled pure xylan from straw at atmospheric pressure (I) and in vacuo (II).

	I	II
Charcoal	31.6	31.5
Tar	6.7	21.4
Pyroligneous acid	43.8	20.1
Gas	18.0	27.0

The distillates contained 7.5 and 6.6 per cent of acid calculated as acetic acid, though neither formic nor acetic acid could be detected, and 6.0 and 2.18 per cent of furfural, respectively. The syrupy distillate from 200 grams of xylan distilled in vacuo gave 1 gram of a crystalline compound, $C_5H_6O_3$, m.p. 206.5°, that probably represents a dehydration product of xylan.

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[1] E. Heuser and G. Jayme, *J. prakt. Chem.*, **105** (1923), 232–242.

[2] H. Bergström, *Papier-Fabr.*, **11** (1913), 759.

[3] E. Heuser and A. Scherer, *Brennstoff-Chem.*, **4** (1923), 97–101.

Esters and Ethers.—Xylan from beech and acacia woods, subjected to acetolysis with acetic anhydride and sulphuric acid, gave only amorphous products.[1] Bader[2] obtained mono- and diacetyl derivatives of wood gum, but more than two acetyl groups could not be introduced. The Schotten-Baumann method gave a monobenzoyl derivative as a crumbly, amorphous mass. A higher benzoyl derivative could not be obtained.

Komatsu and Kashima[3] found that the xylan from wheat straw acetylated readily, giving mono- and diacetyl derivatives. In marked contrast, the xylan from corncobs could scarcely be acetylated by the action of acetic anhydride and acetyl chloride, with and without catalysts. Straw xylan had the rotation $[\alpha]_D = -78°$ in a 2.5 per cent solution of caustic soda. It gave only a trace of xylose on heating with water at 145° for 3 hours. The xylan from corncobs had the rotation $[\alpha]_D = -80°$.

Beech-wood gum, nitrated[4] at 0° with 10 parts of nitric acid of sp. gr. 1.52, swelled but did not dissolve during 24 hours. It contained 12.31 per cent of nitrogen, thus agreeing with a dinitrate. The ester was insoluble in the usual solvents, such as acetone and ethyl acetate.

The nitration of pure xylan from straw cellulose[5] is slight with an acid weaker than

$$HNO_3 : H_2SO_4 : H_2O = 25.10 : 66.85 : 8.05.$$

There was obtained a yield of 115.7 per cent of xylan nitrate containing 8.76 per cent of nitrogen. Of this ester, 61 per cent was soluble in ether-alcohol mixture and contained 7.13 per cent of nitrogen. The remainder was soluble in ethyl and amyl acetates and contained 9.22 per cent of nitrogen.

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[1] G. Zemplén, *Z. physiol. Chem.*, **85** (1913), 182.

[2] R. Bader, *Chem. Ztg.*, **19** (1895), 55.

[3] S. Komatsu and K. Kashima, Mem. Coll. Sci. *Kyoto Imp. Univ.*, **5** (1922), 307–314.

[4] W. Will and F. Lenze, *Ber.*, **31** (1898), 89; *cf.* R. Bader, *l.c.*

[5] B. Rassow and E. Dörr, *J. prakt. Chem.*, **108** (1924), 144.

Xylan dissolved in sodium hydroxide will accept only 1 to 1.5 methyl groups when treated with dimethyl sulphate.[1] The product partially methylated in this way is completely converted into the dimethyl ether, softening at 65 to 70°, by heating with methyl iodide and silver oxide at 100°.

Araban.—Araban, or a carbohydrate yielding arabinose, is present in wood. Hauers and Tollens[2] obtained a small amount of arabinose by the hydrolysis of pine wood with a solution of calcium bisulphite at a temperature between 115 and 135°. Arabinose has been identified in the products of hydrolysis of white spruce[3] (*Picea canadensis*), and in the hemicellulose from beech[4] and American white oak.[5] According to Browne,[6] deciduous trees contain 15 to 25 per cent of pentosans consisting of xylan and a small amount of araban.

The lignin isolated from pine wood by means of strong hydrochloric acid contains 4 to 6 per cent of pentosan that is considered as chemically combined with the lignin. According to Hägglund,[7] the pentosan is chiefly araban, and according to Kürschner,[8] xylan. Heuser[9] looks upon the pentosan in lignin as accidental and as due to incomplete hydrolysis, not chemical combination.

Lævulan.—The presence of fructose in the products of hydrolysis of wood has been reported on various occasions, identification being largely based on color reactions. The most reliable evidence is that furnished by Hägglund,[10] who obtained α-methylphenylfructosazone, m.p. 147 to 148°, from sulphite pulp. The pulp contained 2.5 per cent lævulan. Arabinose, fucose, rhamnose, and galactose were absent. Sherrard[11] did not obtain fructose on hydrolyzing white spruce (*Picea canadensis*).

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[1] E. Heuser and W. Ruppel, *Ber.*, **55** (1922), 2084.

[2] R. Hauers and B. Tollens, *Ber.*, **36** (1903), 3319.

[3] E. C. Sherrard and G. W. Blanco, *J. Ind. Eng. Chem.*, **15** (1923), 611.

[4] C. A. Browne and B. Tollens, *Ber.*, **35** (1902), 1466.

[5] M. H. O'Dwyer, *Biochem. J.*, **17** (1923), 501.

[6] C. A. Browne, "Handbook of Sugar Analysis," N. Y. (1912), p. 553.

[7] E. Hägglund, *Ber.*, **56** (1923), 1866; E. Hägglund and C. J. Malm, *Cellulosechemie*, **4** (1923), 73.

[8] K. Kürschner, *Naturprodukte*, **24** (1923), 36.

[9] E. Heuser, *Cellulosechemie*, **4** (1923), 77.

[10] E. Hägglund and F. W. Klingstedt, *Cellulosechemie*, **5** (1924), 57.

[11] E. C. Sherrard and G. W. Blanco, *J. Ind. Eng. Chem.*, **15** (1923), 612.

There is no satisfactory datum that wood contains a hemicellulose giving glucose on hydrolysis.

Mannan.—In 1889, Tollens[1] obtained from wood (species not stated) what appeared to be mannose hydrazone. Subsequent investigations have shown that mannan is widely distributed in woods and is especially characteristic of the gymnosperms. Bertrand[2] states that in the gymnosperms mannan occupies the place of xylan in the hardwoods. Mannose was obtained from the *Cycadeæ* and *Coniferæ*, but it was absent or nearly so in the *Gnetaceæ*, which are not true gymnosperms.

Tollens[3] and his associates found mannose in sulphite liquor, the raw material generally employed being spruce (*Picea excelsa* Lk.). Mannan occurs not only in the wood[4] of this species, but in the needles[5] and seeds as well.

Mannan was found by Storer[6] in the wood of white pine (*Pinus strobus*); pitch pine (*Pinus rigida*); Norway spruce (*Picea excelsa*); Japanese larch (*Larix leptolepis*); hemlock (*Tsuga canadensis*); red cedar (*Juniperus virginiana*); and white cedar (*Chamæcyparis thyoides*). An extensive investigation of American species renders it highly probable that mannan occurs in all the gymnosperms.

No regularity appears to exist in the amount of mannan occurring in wood when age, season, and the same and different species are considered. Storer[7] obtained 3.61 per cent of mannose from a white pine felled in August and 1.86 per cent from one felled in December. It is improbable that there is a seasonal variation in the mature wood, though he states that pine trees contain much more mannan in late summer than in early winter.

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[1] H. Wheeler and B. Tollens, *Ber.*, **22** (1889), 1046.

[2] G. Bertrand, *Compt. rend.*, **129** (1899), 1025.

[3] J. B. Lindsey and B. Tollens, *Ann.*, **267** (1892), 349; *Ber.*, **23** (1890), 2990; *Z. angew. Chem.*, **5** (1892), 155.

[4] P. Klason, "Zusammensetzung des Fichtenholzes," Berlin (1911), p. 33.

[5] J. B. Lindsey and B. Tollens, *Z. angew. Chem.*, **5** (1892), 154.

[6] F. H. Storer, *Bull. Bussey Inst.*, **3** (1902), 13–45, 47–69.

[7] F. H. Storer, *l.c.*, 37, 51.

MANNAN IN WOODS

SPECIES	MANNAN, PER CENT	
Douglas fir (*Pseudotsuga taxifolia* Briton)	6.65	[1]
Corkbark fir (*Abies arizonica* Merr.)	6.57	
Western larch (*Larix occidentalis* Nutt.)	5.13	
Arborvitæ (*Thuja occidentalis* Linn.)	1.44	
White spruce (*Picea canadensis* Mill.)	7.12	
Longleaf pine (*Pinus palustris* Mill.)	4.75	
Loblolly pine (*Pinus tæda* Linn.)	5.10	
Sugar pine (*Pinus lambertiana* Dougl.)	4.67	
Coulter pine (*Pinus coulteri* Lamb.)	5.22	
Monterey pine (*Pinus radiata* Don.)	7.68	
Piñon pine (*Pinus edulis* Engelm.)	6.00	
California swamp pine (*Pinus muricata* Don.)	3.07	
Chihuahua pine (*Pinus chihuahuana* Engelm.)	5.00	
Western white pine (*Pinus monticola* Dougl.)	6.93	
Whitebark pine (*Pinus albicaulis* Engl.)	4.22	
Western yellow pine (*Pinus ponderosa scopulorum* Englm.)	4.64	
Jeffrey pine (*Pinus jeffreyi*)	5.40	
Digger pine (*Pinus sabiniana* Dougl.)	7.17	
Limber pine (*Pinus flexilis* James)	5.94	
Bristlecone pine (*Pinus aristata* Engelm.)	5.41	
Knobcone pine (*Pinus attenuata* Lemm.)	3.57	
Cryptomeria japonica Don	6.35	[2]
Redwood (*Sequoia sempervirens* Endl.)	3.21	[3]
Western yellow pine (*Pinus ponderosa* Laws.)	6.37	
Sugar pine (*Pinus lambertiana* Dougl.)	6.63	
Taxus baccata Linn	9.10*	[4]
Cupressus torulosa Don	3.4	
Abies pectinata D.C	9.6	
Araucaria brasiliana A. Rich	9.5	
Pinus laricio Poir., cone	8.4	

* As mannose.

[1] A. W. SCHORGER, *J. Ind. Eng. Chem.*, **9** (1917), 748.

[2] C. KIMOTO, *Bull. Coll. Agr. Japan*, **5** (1902), 254.

[3] W. H. DORE, *J. Ind. Eng. Chem.*, **12** (1920), 476.

[4] G. BERTRAND, *Compt. rend.*, **129** (1899), 1025.

Examination[1] of a radial section of a sugar pine 4 feet in diameter showed that the sapwood contained 4.25 per cent mannan and the heartwood from 4.58 to 4.80 per cent. The mannan content of the sapwood in some species is higher than that of the heartwood:

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[1] A. W. SCHORGER, *J. Ind. Eng. Chem.*, **9** (1917), 748.

Species	Mannan content, per cent	
	Sapwood	Heartwood
Cuban pine	9.22	5.81
Western white pine	7.44	7.13
Coulter pine	6.28	5.40

Nor does it follow that the youngest wood is the richer; a longleaf pine sapling 6 years old contained 1.64 per cent mannan in comparison with 4.75 per cent for a mature tree.

No mannose was found in a sound pine log that had been buried in a swamp for 200 years, or in decayed and weathered pine wood taken from the surface.[1]

Hägglund[2] hydrolyzed spruce wood in two ways:

I. Heated with 0.5 per cent sulphuric acid at 155 to 165° for 30 minutes; yield of sugar as glucose 9 per cent.

II. Heated with 0.5 per cent sulphuric acid at 170° for 45 minutes; yield of sugar as glucose 14.5 per cent.

Mannose was the principal sugar formed, as shown by the following table:

Sugar	I, per cent	II, per cent
Xylose	32.7	30.1
Mannose	35.6	43.7
Fructose	4.3	4.7
Galactose	3.3	3.3
Glucose	0.5	14.0
Undetermined	23.6	4.2

He believed that only the hemicelluloses were hydrolyzed in experiment I, the cellulose being attacked with increasing time and temperature.

Mannan appears to occur sparingly in some hardwoods and to be absent in others. The evidence shows irregularity. Mannose has been obtained from the hemicellulose of white oak.[3] Early papers[1] record the presence of mannose in the hydrolyzate from aspen (*Populus tremula*), but Heuser and Brötz[2] have recently reported its absence. It was not found by Schorger[3] or Storer[4] by the direct hydrolysis of a number of deciduous woods, including *Populus tremuloides;* nor by Dore[5] in California live oak (*Quercus agrifolia* Née.).

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[1] F. H. Storer, *Bull. Bussey Inst.*, **3** (1903), 69.

[2] E. Hägglund, *Biochem. Z.*, **70** (1915), 425.

[3] M. H. O'Dwyer, *l.c.*, 501.

Mannose was obtained from the inner bark of several conifers but not from that of *Betula populifolia* and *Populus tremuloides.*[6]

Galactan.—Koch,[7] in 1886, obtained a small amount of mucic acid by oxidizing wood gum with nitric acid, thus showing the presence of a galactose compound. Galactose was subsequently found in sulphite liquor,[8] the woods usually cooked being coniferous. In the sulphite liquor from *Pinus sylvestris,* Hägglund[9] found 0.27 per cent of galactose, based on the wood.

Storer[10] states that he was unable to detect much, if any, galactan in the wood of trees.

In 1916, it was shown by Schorger and Smith[11] that galactans are characteristic of the conifers and unique among wood carbohydrates in being very easily soluble in water. It remains to be seen if the various species of woods contain the same galactan.

Only the ϵ-galactan of the western larch (*Larix occidentalis* Nutt.) has been extensively studied. A gum-like excrescence of the western larch had been examined, but not identified, by Trimble.[12] The galactan content of the wood varies from 8 to 17 per cent. To isolate it, the aqueous extract is first purified by adding tannic acid, then an excess of lead acetate, and filtering. The excess lead is removed with hydrogen sulphide. On adding an excess of alcohol to the clear, concentrated filtrate, the galactan is precipitated as a gummy mass that soon becomes granular.

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[1] K. Fromherz, *Z. physiol. Chem.*, **50** (1906), 237; W. Koch, Diss. Freiburg (1909), 7.

[2] E. Heuser and A. Brötz, *Papier-Fabr. Fest u. Auslandsheft*, 23 (1925), 69.

[3] A. W. Schorger, *l.c.*

[4] F. H. Storer, *Bull. Bussey Inst.*, **3** (1902), 32, 53, 108.

[5] W. H. Dore, *J. Ind. Eng. Chem.*, **12** (1920), 984.

[6] F. T. Dillingham, *Bull. Bussey Inst.*, **3** (1906), 127, 128.

[7] F. Koch, *Pharm. Z. Russl.*, **25** (1886), 668.

[8] T. Seliwanoff, *Chem. Zentr.*, **60,** I (1889), 549; J. B. Lindsey and B. Tollens, *Z. angew. Chem.*, **5** (1892), 154; H. Krause, *Chem. Ind.*, **29** (1906), 217.

[9] E. Hägglund, *Biochem. Z.*, **70** (1915), 416.

[10] F. H. Storer, *Bull. Bussey Inst.*, **3** (1902), 39.

[11] A. W. Schorger and D. F. Smith, *J. Ind. Eng. Chem.*, **8** (1916), 494.

[12] H. Trimble, *Am. J. Pharm.*, **70** (1898), 152.

Pure ϵ-galactan forms a white powder that dissolves easily in cold water to form a mobile liquid. The rotation is $[\alpha]_D^{20°} = +12.11°$. The galactan gave 6.18 per cent of furfural, but no sugar other than galactose could be identified. Ultimate analysis and a molecular-weight determination by the freezing-point method gave the formula $(C_6H_{10}O_5)_{20}$. The acetyl derivatives were amorphous.

Galactan has been identified in the following hardwoods: aspen (*Populus tremula*);[1] white oak;[2] apple wood;[3] California live oak (*Quercus agrifolia*).[4]

According to Salkowski,[5] galactan is not precipitated by Fehling's solution and appears to be destroyed by heating with alkalis, even ammonia.

Wood Cellulose.—The cotton hair is unique in consisting almost entirely of orthoglucosan, *i.e.*, glucose anhydride,[6] and is universally recognized as the source for standard cellulose. It is entirely possible that celluloses exist in which mannan or xylan is chemically combined with the orthoglucosan. One school holds to the opinion that all celluloses when properly purified are identical with cotton cellulose; another, that there are celluloses containing the anhydrides of several different sugars. The mode of linkage, if any, between orthoglucosan and xylan or mannan is problematical, though, reasoning from analogy, it would probably be glucosidal.

Cellulose has been defined in various ways. In order to have a concrete working basis, Schorger[7] defined wood cellulose as the residue remaining after alternate treatment of wood with chlorine gas and sodium suphite to the point where the chlorine-sodium sulphite, or the Mäule reaction for lignin, ceases.

[1] K. Fromherz, *Z. physiol. Chem.*, **50** (1906), 238.

[2] M. H. O'Dwyer, *l.c.*

[3] W. E. Tottingham *et al.*, *J. Biol. Chem.*, **21** (1920), 407.

[4] W. H. Dore, *J. Ind. Eng. Chem.*, **12** (1920), 984.

[5] E. Salkowski, *Z. physiol. Chem.*, **34** (1901), 175, 177.

[6] A. W. Schorger, *J. Ind. Eng. Chem.*, **16** (1924), 141.

[7] A. W. Schorger, *J. Ind. Eng. Chem.*, **9** (1917), 561.

Klason[1] has recently defined cellulose as the carbohydrate residue that does not dissolve at 98° in a solution containing 13 grams of free and 37 grams of half-bound sulphur dioxide per liter. He finds that when wood is digested with sulphite liquor under the above conditions, the yield of cellulose remains constant, even though the digestion be prolonged with fresh liquor. Wood cellulose will also withstand a liquor containing 32 grams of sulphur dioxide, its fibrous structure being retained. Cotton behaves quite differently with the stronger acid. Only 90.5 per cent of the cellulose is recovered, and this is in a structureless form similar to hydrocellulose.

The term "cellulose" has been used by Cross[2] "as the comprehensive expression for the non-nitrogenous basis of the vegetable world." This definition embraces the simple and compound celluloses and is perhaps satisfactory from a botanical viewpoint.

There are many adherents to the theory that the normal cellulose of wood contains adsorbed hexosans and pentosans. The adsorption theory has been developed at length by Wislicenus[3] to account for plant growth. Just how colloids can be synthesized by the cell protoplasm and transferred to the cell wall for adsorption is not at all clear.

According to Wise,[4] cellulose consists of small units arranged, for the purpose of illustration, like bricks in a wall. The units are held together by primary and secondary valencies. Wood cellulose is to be distinguished from cellulose only by the presence of variable amounts of adsorbed carbohydrates.

Herzog and Jancke[5] obtained identical Röntgen-ray spectrograms from cotton, ramie, linden wood, and wood pulp, indicating that the same cellulose occurs in each.

The opinion is held by Heuser[6] that all plant celluloses, regardless of their source, are identical. Bleached coniferous cellulose was purified by boiling three times with 6 per cent sodium

[1] P. Klason, *Papier-Fabr.*, **22** (1924), 373.

[2] C. F. Cross, in: "Chemistry in the Twentieth Century," N. Y. (1924) p. 159.

[3] H. Wislicenus and M. Kleinstück, *Kolloid Z.*, **6** (1910), 17, 87.

[4] L. E. Wise, *J. Ind. Eng. Chem.*, **15** (1923), 711.

[5] R. O. Herzog and W. Jancke, *Ber.*, **53** (1920), 2162.

[6] E. Heuser and E. Boedeker, *Z. angew. Chem.*, **34** (1921), 461; E. Heuser and A. Haug, *Ibid.*, **31** (1918), 173.

hydroxide or, as an alternative, extracted with cold 17 per cent sodium hydroxide. In this way the pentosan content was reduced from 4.06 to 1.92 per cent. The purified cellulose and cotton were hydrolyzed with strong hydrochloric acid for comparison; in both cases the maximum dextrose reading was obtained after 16.5 hours. From the wood cellulose, 94.2 per cent of dextrose was isolated in the pure condition.

The identity of wood cellulose with cotton cellulose has been claimed[1] on the ground of having obtained comparable yields of cellobiose octacetate after the wood cellulose had been freed from pentosans with 17.5 per cent sodium hydroxide.

The action of boiling 6 per cent, or cold 17.5 per cent sodium hydroxide, is too severe to permit conclusions to be drawn concerning adsorption or chemical combination. The same may be said of acetolysis when applied to the crude or purified wood cellulose. The splitting off of pentosans could readily occur with any of these reagents.

It is a question whether the formation of cellobiose octacetate is a criterion for the identity of celluloses. The lichenin from Iceland moss (*Cetraria islandica*) gives cellobiose octacetate, acetobromocellobiose, and a triacetate having a rotation ($[\alpha]_D^{19°} = -23.8°$) very similar to cellulose triacetate;[2] and when distilled rapidly at 12-millimeters pressure, lævoglucosan[3] is obtained. Lichenin, nevertheless, is soluble in dilute alkali and gives a clear colloidal solution with boiling water. Furthermore, it hydrolyzes readily with dilute acids at atmospheric pressure, giving 64.86 per cent of dextrose.[4]

Lichenin from its ease of hydrolysis would, accordingly, correspond to Schulze's definition of a hemicellulose. Salkowski[4] believes that the degree of hydrolysis depends on the physical condition of the carbohydrate; the more finely it is divided the more drastic is the action. This case illustrates the difficulty in drawing a line between a cellulose and a hemicellulose. Karrer[5] considers lichenin to be a "reserve" cellulose (hemicellulose), as it is quantitatively converted to dextrose by the enzyme lichenase found in the snail, *Helix pomatia.* Cotton is scarcely attacked.

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[1] L. E. Wise and W. C. Russell, *J. Ind. Eng. Chem.*, **14** (1922), 285; **15** (1923), 815; *cf.* S. V. Hintikka, *Cellulosechemie*, **4** (1923), 62.

[2] P. Karrer and B. Joos, *Biochem. Z.*, **136** (1923), 537; *Helvetica Chim. Acta*, **6** (1923), 800; P. Karrer and K. Nishida, *Ibid.*, **7** (1924), 363.

[3] P. Karrer and M. Staub, *Helvetica Chim. Acta*, **7** (1924), 928.

[4] E. Salkowski, *Z. physiol. Chem.*, **114** (1921), 31.

[5] P. Karrer *et al.*, *Helvetica. Chim. Acta*, **6** (1923), 800; **7** (1924), 144, 518.

The identity of "normal" celluloses may also be questioned. The cellulose isolated from marine fiber (*Posidonia australis*) is regarded as consisting, like cotton, of glucose anhydride residues. The optical rotations of their triacetates, however, differ greatly, as shown by the following:

	$[\alpha]_D$
Cotton triacetate	−22.3°
Posidonia triacetate	−39.8°

This variation indicates a difference in chemical structure.[1]

Esparto cellulose, according to Irvine and Hirst,[2] behaves as a mixture or solid solution containing 81.5 per cent normal cellulose and 18.5 per cent xylan. On being freed from xylan, esparto cellulose acts like cotton cellulose, giving cellobiose octacetate and 2, 3, 6-trimethylglucose. It is noteworthy that in no case was cellobiose octacetate obtained from the cellulose that had not been freed from xylan by alkaline extraction.

The approximately complete elimination of pentosans from wood or straw cellulose is accompanied by a considerable loss of cellulose due to the persistence with which the pentosans are retained. Straw cellulose[3] isolated by the chlorine method gave 10.30 per cent furfural (22.34 per cent xylan). After six extractions with hot 6 per cent sodium hydroxide, the residue gave 1.97 per cent furfural. Heuser found it difficult, if not impossible, to free the cellulose completely from xylan. Nor could the xylan be eliminated by treating the straw directly with sodium hydroxide; after five treatments the residue (40 per cent) contained 9.69 per cent xylan. Treatment of the residue with chlorine did not reduce the amount of xylan.

Heuser[4] remarks that nearly complete elimination of pentosans would be expected through digesting straw with caustic soda at a pressure corresponding to 140 to 150°. It is a surprising fact, however, that the straw pulp retains 29 per cent of xylan.

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[1] J. C. Earl, *J. Chem. Soc.*, **125** (1924), 1322.

[2] J. C. Irvine and E. L. Hirst, *J. Chem. Soc.*, **125** (1924), 15–25; *cf.* E. L. Hirst, *J. Soc. Chem. Ind.*, **41** (1922), 392R.

[3] E. Heuser and A. Haug, *Z. angew. Chem.*, **31** (1918), 166–168.

[4] E. Heuser, *l.c.*, 168.

In the case of sulphite wood pulp, after two extractions with 17 per cent sodium hydroxide, the pentosans were distributed as follows:

	Pentosans, Per Cent
α-Cellulose	0.8
β-Cellulose	1.26
γ-Cellulose	2.16

There is, accordingly, no way of telling if the hemicelluloses and cellulose are combined or not.[1]

Hydrolysis of purified straw cellulose with 72 per cent sulphuric acid gave results in close agreement with those for cotton, thus affording evidence that the two celluloses are identical in constitution.[2] Wood cellulose is also identical with cotton in that it gives comparable yields of cellulose triacetate, α-methylglucoside, and crystalline dextrose.[3] There is no difficulty in agreeing with these conclusions, based on the purified cellulose, but the relation of the original hexosans and pentosans to the residual cellulose is still unexplained.

As might be expected, pentosans are removed with greater difficulty from lignocellulose than from the isolated cellulose. Fromherz[4] purified aspen wood with 5 per cent hydrochloric acid, water, alcohol, ether, and 5 per cent ammonia. It was then extracted six times with 10 per cent sodium hydroxide for 36 hours each. In this way about 18 per cent of wood gum was obtained, though the wood lost 45 per cent in weight by the treatment. The residual wood gave 2.29 per cent furfural and 0.5 per cent "methylfurfural."

Extraction of pentosans with dilute sodium hydroxide rapidly reaches a maximum when the wood is simultaneously ground to a gelatinous condition.[5] When the wood was ground with an added solution of pentosans, no adsorption of pentosans took place, though its gelatinous condition presumably should have favored this phenomenon.

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[1] E. Heuser and W. Dammel, *Cellulosechemie*, **5** (1924), 45.

[2] E. Heuser and A. Haug, *Z. angew. Chem.*, **31** (1918), 172.

[3] E. Heuser and S. S. Aiyar, *Z. angew. Chem.*, **37** (1924), 27.

[4] K. Fromherz, *Z. physiol. Chem.*, **50** (1906), 209.

[5] A. W. Schorger, *J. Ind. Eng. Chem.*, **16** (1924), 141.

It is conceivable that if the carbohydrates are adsorbed, their colloidal state might render extraction with alkalis slow and incomplete. This argument cannot, however, explain the difficulty encountered in removing pentosans by acid hydrolysis. Winterstein[1] heated beech wood, containing 26.46 per cent of xylan, with 1.25 per cent sulphuric acid for 3 hours. The wood lost 17.75 per cent in weight but the residue contained 18.46 per cent of pentosans. After 3 hours' heating with 5 per cent acid, it still contained 10.16 per cent of xylan. Beech-wood cellulose isolated with F. Schulze's reagent retained 21.83 per cent of the xylan originally present. A second treatment did not lower the xylan content. Similar results were obtained by Schulze.[2] Winterstein concluded that xylan is present in wood in two different forms, the one being destroyed by boiling, dilute acid, and F. Schulze's reagent, while the other is resistant; and that some of the xylan is chemically combined with the cellulose.

A similar conclusion had been reached by Schulze and Tollens,[3] as a result of the difficulty experienced in removing pentosans from spent malt. The latter, after boiling with 4 per cent sulphuric acid for 6 hours, followed by extraction with 5 per cent sodium hydroxide, still contained pentosans.

Wheat-bran cellulose yields furfural even after being submitted to drastic chemical reactions. Sherman,[4] therefore, concludes that about 10 per cent of pentosan is combined with the cellulose.

According to Kunz[5] barley chaff contains two kinds of pentosans. The one is easily hydrolyzed by heating for several hours with 2 per cent sulphuric acid; the other with difficulty, heating with 1 per cent acid at 3 to 4 atmospheres' pressure being required.

Nitrated wood and straw celluloses of high pentosan content contain considerable amounts of unnitrated material. This condition is attributed to formation by the pentosans of a hard, protective coating around the fibers.[1] Local concentration of pentosans would be very strong proof against chemical combination, but such a condition has not been established.

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[1] E. Winterstein, *Z. physiol. Chem.*, **17** (1893), 381.

[2] E. Schulze, *Z. physiol. Chem.*, **16** (1892), 435.

[3] E. Schulze and B. Tollens, *Ann.*, **271** (1892), 55.

[4] H. C. Sherman, *J. Am. Chem. Soc.*, **19** (1897), 300.

[5] E. Kunz, *Biochem. Z.*, **74** (1916), 312.

Evidence has been introduced that mannocelluloses exist. Schulze[2] called coffee-bean cellulose a mannocellulose, since after boiling with dilute hydrochloric acid, followed by treatment with F. Schulze's reagent, (20 parts of nitric acid, sp. gr. 1.16, and 3 parts potassium chlorate), it still contained mannose. Mannocellulose from coffee beans, sesame cake, and coconut cake is not destroyed by F. Schulze's reagent, Hoffmeister's reagent ($HCl + KClO_3$), Lifschutz's mixture of sulphuric and nitric acids, nor by heating with caustic alkali at 180°; hence it should be considered as similar to cellulose.[3]

According to Gilson,[4] the mannocellulose of Schulze does not exist as a chemical entity but as a mixture that can be separated into mannan and cellulose. Coffee beans, purified with dilute acids and alkalis, were dissolved in cuprammonium solution. On treating this solution with carbon dioxide for 15 minutes, the cellulose formed a gelatinous precipitate, while mannan remained in solution. If mannan exists as such, it is difficult to understand how it resists the drastic chemical treatment to which it was submitted by Schulze unless the carbohydrate mixture was in such coarse particles that the mannan was very slowly attacked.

The status of the mannan in wood is less doubtful. Bertrand,[5] for no apparent reason, considered the mannose of the conifers to exist as a mannocellulose. This view is supported by Sherrard,[6] since mannose persists in sulphite pulp, Cross and Bevan cellulose, and the α-, β-, and γ-celluloses. Mannose was not obtained from cotton on hydrolysis, showing that mannose residues must preexist in wood. Schorger[7] had found that mannose could be quantitatively hydrolyzed from wood by the aid of boiling dilute mineral acids; therefore, unless Schulze's definition be discarded, the mother substance of the mannose must be classed as a hemicellulose. Heuser[1] does not consider mannan as chemically combined with cellulose in sulphite pulp, since the greater portion can be removed by extracting the pulp two or three times with 17 per cent sodium hydroxide.

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[1] B. Rassow and E. Dörr, *J. prakt. Chem.*, **108** (1924), 113.

[2] E. Schulze, *Z. physiol. Chem.*, **16** (1892), 425.

[3] E. Schulze, *Z. physiol. Chem.*, **19** (1894), 38.

[4] E. Gilson, *La Cellule*, **9** (1893), 428.

[5] G. Bertrand, *Compt. rend.*, **129** (1899), 1025.

[6] E. C. Sherrard and G. W. Blanco, *J. Ind. Eng. Chem.*, **15** (1923) 615; E. C. Sherrard and A. W. Froehlke, *J. Am. Chem. Soc.*, **45** (1923), 1729.

[7] A. W. Schorger, *J. Ind. Eng. Chem.*, **9** (1917), 748.

The very interesting observation has recently been made by Sherrard[2] that white-spruce cellulose, as ordinarily prepared by the Cross and Bevan method, may contain as much as 20 per cent of a material extractable by boiling water. It may be isolated in the form of a white, extremely hygroscopic powder, having a relatively low reducing value. The powder on hydrolysis gives about 30 per cent of mannose and 20 per cent of pentose. The compound has been obtained in a partially crystalline state, but whether it consists of a definite body or a mixture remains to be determined. The mannose removed by water extraction constitutes about 43 per cent of that contained in the original cellulose.

It is apparent that the relation of certain hexosans and pentosans to the "normal cellulose" in wood is still only a matter of individual opinion. No convincing arguments or experimental data, for or against chemical combination, have been produced.

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[1] E. Heuser and W. Dammel, *Cellulosechemie*, **5** (1924), 45.

[2] E. C. Sherrard and G. W. Blanco, *J. Ind. Eng. Chem.*, **15** (1923), 1166.

CHAPTER VI

THE CONSTITUTION OF CELLULOSE

Cellulose can be hydrolyzed to glucose in practically quantitative yield, showing that it consists entirely of anhydroglucose units. Each unit contains three free hydroxyl groups, one of which is primary, the remainder secondary. Their position is established by the formation of 2, 3, 6-trimethylglucose. Acetolysis of cellulose gives from 35 to 60 per cent of cellobiose, indicating that the glucose units are united wholly or in large part by cellobiose linkages. Cellulose is probably a polycyclic compound and should be represented as $(C_6H_{10}O_5)_n$, not $(C_6H_{10}O_5)_n \cdot H_2O$.[1] The number of units in the molecule or aggregate is entirely unknown. Cellulose shows a high optical activity in cuprammonium solution, but this has no bearing on its structure. Röntgen-ray spectrograms of cellulose fibers indicate a crystalline structure.

Acetolysis of Cellulose.—Acetolysis represents a reaction wherein the hydroxyl groups formed by the splitting of ether linkages are acetylated[2] and may be considered as simultaneous hydrolysis and acetylation. Acetolysis is usually conducted with acetic anhydride, or acetyl bromide and chloride in the presence of catalysts, such as phosphorus trichloride, zinc chloride, sulphuric acid, and anhydrous sodium acetate. The products formed in the acetolysis of cellulose depend on the nature and amount of the catalyst and the degree of heating.

In 1879 Franchimont[3] acetylated cellulose, obtaining a compound containing 68.5 per cent acetic acid and melting at 212°.

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[1] H. Kiliani, *Chem. Ztg.*, **32** (1908), 366; P. Bary, *Compt. rend.*, **178** (1924), 1159.

[2] E. Knoevenagel, *Ann.*, **402** (1914), 113.

[3] A. P. N. Franchimont, *Ber.*, **12** (1879), 1941–1942.

Saponification of this derivative gave a new disaccharide at first called cellose,[1] then cellobiose,[2] to distinguish it from the monoses. Up to this time, no sugar higher than glucose had been obtained from cellulose, and the potential importance of cellobiose in relation to the constitution of cellulose was immediately recognized. Acetolysis in the presence of sulphuric acid[2] gives α-cellobiose octacetate, and of sodium acetate,[3] β-cellobiose octacetate. The β-form can be converted into the α-form by heating with acetic anhydride in the presence of a small amount of sulphuric acid,[4] or preferably zinc chloride.[5] The β-form can also be obtained from acetochloro-cellobiose with silver acetate.[6] The production of α-cellobiose octacetate is no indication that it is derived from either α- or β-cellobiose in the cellulose molecule, since either form would yield the same α-octacetate.[5]

To prepare cellobiose octacetate, 10 grams of air-dry cotton are gradually added to a cooled mixture of 40 grams of acetic anhydride and 5 grams of concentrated sulphuric acid, care being taken that the temperature does not exceed 40 to 50°. Let stand at room temperature. Complete solution of the cellulose takes place in a few hours and crystallization of the cellobiose octacetate is complete in 6 to 7 days. The crystalline paste is warmed with 60 cubic centimeters of glacial acetic acid and poured into 1500 cubic centimeters of ice water. After standing 30 minutes, filter off the octacetate, dry at 100°, and extract with chloroform. After evaporation of the solvent the residue is crystallized from boiling alcohol.[7] Freudenberg[8] maintains the acetylating solution, containing the cellulose, in a cooling mixture for 8 hours, then in water at room temperature for 12 hours. It is then removed and allowed to stand for 12 days. The yield is 35 to 36 per cent of the theoretical in a single operation.

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[1] Z. H. Skraup and J. König, *Ber.*, **34** (1901), 1115; **32** (1899), 2413.

[2] Z. H. Skraup and J. König, *Monatsh.*, **22** (1901), 1011–1036.

[3] L. Maquenne and W. Goodwin, *Bull. soc. chim.*, [3] **31** (1904), 854–859.

[4] L. Maquenne and W. Goodwin, *l.c.*; E. R. von Hardt-Stremayr, *Monatsh.*, **28** (1907), 63–72.

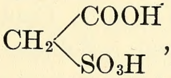
[5] C. S. Hudson and J. M. Johnson, *J. Am. Chem. Soc.*, **37** (1915), 1278.

[6] E. Geinsperger, *Monatsh.*, **26** (1905), 1459.

[7] J. Madsen, "Die Acetolyse der Cellulose zu Cellobiose- und Dextrinacetaten," Diss. Hanover (1917), 53 pp.

[8] K. Freudenberg, *Ber.*, **54** (1921), 771.

The process may be hastened, at the expense of the yield, by adding 20 grams of air-dry filter paper, cut into strips, to a mixture of 80 cubic centimeters of acetic anhydride and 11 cubic centimeters of concentrated sulphuric acid, the temperature being held just below 20°. The flask is then placed in a calcium chloride bath held at 120° and as soon as the color of the solution changes from red to black, the critical stage, the contents are poured into 1.5 liters of cold water. After standing 6 hours the precipitate is filtered off, dried at 40°, and crystallized from boiling 90 per cent alcohol. The yield is 25 to 35 per cent of the weight of the cellulose.[1]

Air-dry cellulose containing 8 to 10 per cent of moisture should be used. If more water is present, too much heat is generated, while perfectly dry cellulose is not penetrated by the acetylating mixture. Hydrocellulose, owing to its fineness, generally gives better yields than fibrous cellulose. The mixing of the acetic anhydride and sulphuric acid should be done with cooling. Sulphoacetic acid,  $CH_2{<}\begin{matrix}COOH\\SO_3H\end{matrix}$, is a poorer catalyst than the acetylsulphuric acid, $CH_3.COO.SO_3H$, formed at low temperatures.[2] If the acetylation mixture contains less than 3.5 per cent or more than 30 per cent of sulphuric acid, the cellobiose octacetate will not crystallize out.[3]

The yields of cellobiose octacetate are too low to determine if cellulose consists entirely of cellobiose residues. Madsen[4] obtained 32 per cent of cellobiose octacetate directly, this figure being increased to 37 to 43 per cent of the theoretical by recovery from the dextrin acetates. Ost[5] obtained 37.2 per cent of pure cellobiose octacetate and 54.9 per cent of ether-soluble dextrin acetates. Comparable yields were obtained by Freudenberg,[6] who, from a study of the loss of cellobiose by hydrolysis during acetolysis, concluded that cellulose contains at least 60 per cent of cellobiose. A similar conclusion was reached by Karrer and

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[1] W. N. Haworth and E. L. Hirst, *J. Chem. Soc.*, **119** (1921), 197.

[2] W. Schliemann, *Ann.*, **378** (1911), 366–381; Diss. Hanover (1910).

[3] F. Klein, *Z. angew. Chem.*, **25** (1912), 1409–1415.

[4] J. Madsen, *l.c.*

[5] H. Ost, *Ann.*, **398** (1913), 338.

[6] K. Freudenberg, *l.c.*

Widmer.[1] The statement has recently appeared that sulphite pulp gives a 90 per cent yield of cellobiose octacetate.[2]

Cellobiose.—Cellobiose forms fine white crystals of the composition $C_{12}H_{22}O_{11}$, after drying at 100°. It decomposes at 225°. The initial rotation $[\alpha]_D = +26.1°$ becomes constant at $+ 33.7°$.[3] The osazone crystallizes in yellow needles melting at 208 to 210°.[4] The sugar is scarcely affected by yeast. Cellobiase, found in the mycelium of *Aspergillus niger* and in the kernels of apricots and almonds, splits cellobiose into glucose.[5] Taka-diastase[6] contains a cellobiase that hydrolyzes cellobiose completely to glucose in 5 days at a temperature of 37°. Bacteria that ferment cellulose attack cellobiose, but not Ost's "celloisobiose." *Bacillus butylicus* attacks both cellobiose and "celloisobiose."[7]

Cellobiose has been synthesized by the action of emulsin on a mixture of ethylene glycol, dextrose, and aqueous alcohol.[8]

To prepare cellobiose, dissolve 12 grams of potassium hydroxide in 40 cubic centimeters of alcohol at 90°. Cool in a water bath, add 10 grams of finely pulverized cellobiose octacetate with agitation, taking care that the temperature does not exceed 35 to 40°. There separates a viscous mass of the potassium salt of cellobiose. When this has collected together, decant the supernatant liquid, wash the residue twice with strong alcohol, dissolve the remainder in a little warm water, and neutralize exactly with perchloric acid. Filter to remove the potassium perchlorate, concentrate to the point of formation of a thin film, let cool, filter a second time, and concentrate again on the water bath to the point of crystallization. Decant into a small flask, add 3 to 4 volumes of methyl alcohol, and let stand. The follow-

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[1] P. Karrer and F. Widmer, *Helvetica Chim. Acta*, **4** (1921), 174–184.

[2] T. Ozawa, *J. Chem. Ind.* (*Japan*), **27** (1924), 884; *J. Soc. Chem. Ind.*, **44** (1925), B166.

[3] Z. Skraup and J. König, *Ber.*, **34** (1901), 117.

[4] W. Schliemann, *l.c.*, 371.

[5] G. Bertrand and M. Holderer, *Compt. rend.*, **149** (1909), 1385–1387; **150** (1910), 230–232; E. Fischer and G. Zemplén, *Ann.*, **372** (1909), 254–256.

[6] C. Neuberg and O. Rosenthal, *Biochem. Z.*, **143** (1923), 399.

[7] C. Neuberg and R. Cohn, *Biochem. Z.*, **139** (1923), 527.

[8] E. Bourquelot and M. Bridel, *Compt. rend.*, **168** (1919), 1016–1019.

DERIVATIVES OF CELLOBIOSE

Substance	Formula	Melting point	$[\alpha]_D$	Reference
Heptaceto-cellobiose	$C_{12}H_{15}O_4(C_2H_3O_2)_7$	195–197°	+19.95°	4
α-Octaceto-cellobiose	$C_{12}H_{14}O_3(C_2H_3O_2)_8$	229.5	+ 41.95	1
β-Octaceto-cellobiose	$C_{12}H_{14}O_3(C_2H_3O_2)_8$	202	− 14.74	
Hexamethyl-methylcellobioside	$C_{12}H_{14}O_4(OCH_3)_7$	83–84	− 7.73	2
Heptamethyl-methylcellobioside	$C_{12}H_{13}O_3(OCH_3)_8$	86	− 15.91	
Heptaceto-chlorocellobiose	$C_{12}H_{14}O_3(C_2H_3O_2)_7Cl$	195	+ 75.21	3
Heptaceto-bromocellobiose	$C_{12}H_{14}C_3(C_2H_3O_2)_7Br$	180+	+ 96.3	4
Heptaceto-iodocellobiose	$C_{12}H_{14}O_3(C_2H_3O_2)_7I$	160–170	+125.3	
Heptabenzoyl-cellobiose	$C_{12}H_{15}O_4(C_7H_5O_2)_7$	202–204	....	5

[1] C. S. HUDSON and J. M. JOHNSON, *J. Am. Chem. Soc.*, **37** (1915), 1278.

[2] P. KARRER and F. WIDMER, *Helvetica Chim. Acta*, **4** (1921), 182.

[3] Z. H. SKRAUP and E. GEINSPERGER, *Monatsh.*, **26** (1905), 1469.

[4] E. FISCHER and G. ZEMPLÉN, *Ber.*, **43** (1910), 2536.

[5] S. V. HINTIKKA, *Cellulosechemie*, **4** (1923), 62.

ing day collect the cellobiose that has deposited and wash carefully with methyl alcohol. The yield is 3 grams.[1]

Hess,[2] by the action of acetyl chloride on cellulose, and subsequent saponification, obtained an anhydrobiose, $C_{12}H_{20}O_{10}\cdot 2H_2O$, becoming brown at 250° and decomposing at 270°. The sugar was insoluble in water and in ammonia, soluble in the caustic alkalis and in cuprammonium, and reduced Fehling's solution only slightly. It had a marked tendency to association. It was considered as closely related to the structural unit in cellulose. Acetolysis of ethylcellulose[3] gave a tetraethylanhydrobiose, as shown by the molecular weight which was determined in very dilute aqueous solution to prevent association.

The sulpholysis of cellulose with fuming sulphuric acid at 0° gave a sulphate which is apparently a derivative of cellobiose.[4] The crystalline barium salt, $(C_{12}H_{21}O_{10}\cdot SO_4)Ba$, which is obtained in a yield of 50 per cent of the theoretical, is soluble in water, but insoluble in alcohol. It is *d*-rotatory, and reduces Fehling's solution only on warming.

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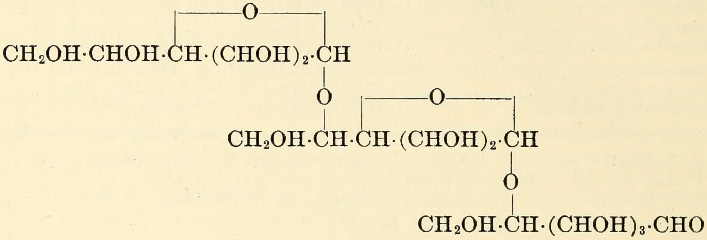
[1] L. MAQUENNE and W. GOODWIN, *Bull. soc. chim.*, [3] **31** (1904), 855.

[3] K. HESS, *Ber.*, **54** (1921), 2867–2885.

[3] K. HESS and W. WITTELSBACH, *Ber.*, **54** (1921), 3232–3241; *cf.* K. HESS *et al.*, *Z. angew. Chem.*, **34** (1921), 449–454.

[4] A. C. VON EULER and K. MELANDER: cited by E. HÄGGLUND, "Die Hydrolyse der Zellulose und des Holzes" (1915), p. 15.

Procellose.—The acetolysis of cellulose, using sulphuric acid as the catalyst, yields also the acetyl derivative of a trisaccharide, procellose.[1] It crystallizes with two molecules of water, melts at 210°, and has the specific rotation $[\alpha]_D = +22.8°$. It contains one aldehyde group. The following constitution is suggested:


O
$CH_2OH{\cdot}CHOH{\cdot}CH{\cdot}(CHOH)_2{\cdot}CH$
O
O
$CH_2OH{\cdot}CH{\cdot}CH{\cdot}(CHOH)_2{\cdot}CH$
O
$CH_2OH{\cdot}CH{\cdot}(CHOH)_3{\cdot}CHO$

The "celloisobiose" of Ost and Prosiegel[2] has been shown to be a mixture of cellobiose and procellose.[3] When the mixture of sugars is shaken for several days at room temperature with 70 per cent alcohol, with daily renewal of the solvent until the amount of sugar dissolved in the solvent becomes constant, the residue consists of procellose which is purified by a recrystallization from 95 per cent alcohol.

Constitution of Cellobiose and Cellulose.—On treating cotton impregnated with 17 per cent sodium hydroxide, in quantity represented by $C_6H_{10}O_5.2NaOH$, with dimethylsulphate, Denham and Woodhouse[4] obtained a product with 24 to 26 per cent methoxyl. Hydrolysis of this methylcellulose by Willstätter's method gave a trimethylglucose (m.p.110°; $[\alpha]_D = +69.52°$), in addition to lower methylglucoses. The trimethylglucose behaved as a uniform body, indicating that the cellulose molecule was symmetrical and contained but three free hydroxyl groups for each C_6 residue. There are four possible trimethylglucoses, each of which can exist in α- and β-form.

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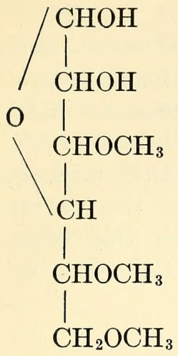
[1] G. Bertrand and S. Benoist, *Compt. rend.*, **176** (1923), 1583–1587.

[2] H. Ost and R. Prosiegel, *Z. angew. Chem.*, **33**, I (1920), 100; H. Ost and G. Knoth, *Cellulosechemie*, **3** (1922), 25.

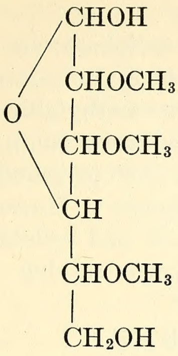
[3] G. Bertrand and S. Benoist, *Compt. rend.*, **177**, (1923) 85–87.

[4] W. S. Denham and H. Woodhouse, *J. Chem. Soc.*, **105** (1914), 2357–2368; **103** (1913), 1735–1742.

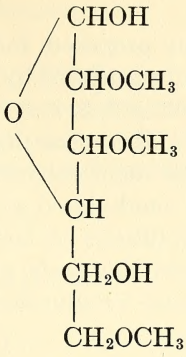
I



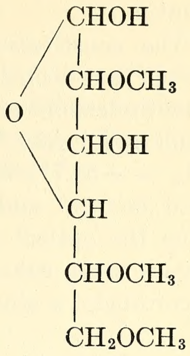
II



III



IV



I. 3, 5, 6-Trimethylglucose.

II. 2, 3, 5-Trimethylglucose; syrup; $[\alpha]_D^{20°} = +42.7° \rightarrow 66.8°$; n_D 1.4780.[1]

III. 2, 3, 6-Trimethylglucose; fine needles or short prisms; m.p. 122 to 123° or 92 to 93°; $[\alpha]_D = +90.2° \rightarrow 70.5°$; $n_D = 1.4743$.[2]

IV. 2, 5, 6- Trimethylglucose.

For establishing the identity of the trimethyl glucose from cellulose, formula (I) is excluded since it can give an osazone, and (II) is known. The trimethylglucose from cellulose on condensation with hydrocyanic acid gave an acid containing only two methoyxl groups. Titration showed that the acid was partially lactonized. On the assumption that a γ-lactone is formed, the methyl group at position 3 must have been split off so that the trimethylglucose would have structure III.[3] The correctness of this formula has been confirmed by Irvine and Hirst.[4]

By repeated methylation it was possible to obtain methylcellulose containing 44.6 per cent methoxyl,[5] the theoretical being 45.6 per cent. Products containing 40 per cent or more of methoxyl are soluble in water but insoluble in cuprammonium solution.

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[1] J. Irvine and J. W. Oldham, *J. Chem. Soc.*, **119** (1921), 1756; *cf.* T. Purdie and R. C. Bridgett, *Ibid.*, **83** (1903), 1037.

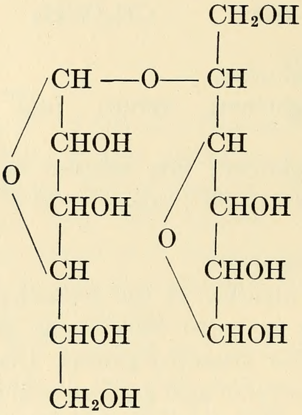
[2] J. C. Irvine and E. L. Hirst, *J. Chem. Soc.*, **121** (1922), 1216.

[3] W. S. Denham and H. Woodhouse, *J. Chem. Soc.*, **111** (1917), 244–249.

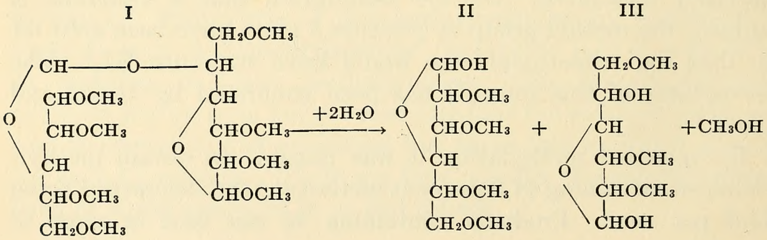
[4] J. C. Irvine and E. L. Hirst, *J. Chem. Soc.*, **121** (1922), 1217.

[5] W. S. Denham, *J. Chem. Soc.*, **119** (1921), 77–81.

The constitution proposed for cellobiose by Haworth and Leitch[1] has been substantiated by the hydrolysis of heptamethyl-β-methylcellobioside to 2, 3, 5, 6-tetramethylglucose, and 2, 3, 6-trimethylglucose.[2] The trimethylglucose (m.p. 115 to 116°; $[\alpha]_D = +68.7°$) was identical with that prepared from methylated lactose[3] and methylated cellulose.[4] Hudson[5] had shown from the optical rotations of lactose and cellobiose that these sugars must contain the same glucose residue. Cellobiose is, accordingly, a glucose-5-β-glucoside.



Cellobiose



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[1] W. N. Haworth and G. C. Leitch, *J. Chem. Soc.*, **115** (1919), 813.

[2] W. N. Haworth and E. L. Hirst, *J. Chem. Soc.*, **119** (1921), 193; P. Karrer and F. Widmer, *Helvetica Chim. Acta*, **4** (1921), 295; *cf.* M. Bergmann, *Naturwiss.*, **9** (1921), 308.

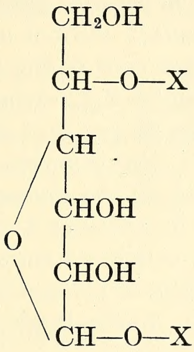
[3] W. N. Haworth and G. C. Leitch, *J. Chem. Soc.*, **113** (1918), 188.

[4] W. S. Denham and H. Woodhouse, *J. Chem. Soc.*, **105** (1914), 2364.

[5] C. S. Hudson, *J. Am. Chem. Soc.*, **38** (1916), 1573.

1. Heptamethyl-β-methylcellobioside.
II. 2, 3, 5, 6-Tetramethylglucose.
III. 2, 3, 6-Trimethylglucose.

The formation of 2, 3, 6-trimethyglucose led Haworth and Hirst[1] to suggest for cellulose the structure given below, in which X represents additional glucose anhydride groups. The same structure was simultaneously proposed by Hibbert.[2]



Cellulose
(Unit group)

It had been shown by Monier-Williams[3] that hydrolysis of cellulose with 72 per cent sulphuric acid yielded 91 per cent of crystalline glucose. Furthermore, acetolysis of cellulose, followed by simultaneous hydrolysis and formation of methylglucoside through the heating of the acetylated products with methyl alcohol and hydrogen chloride, gave 85 per cent of the theoretical yield of methylglucoside.[4] On repeating the acetolysis with sulphuryl chloride as the catalyst, a practically quantitative yield of pure cellulose triacetate was obtained. The triacetate was converted into an equilibrium mixture of α- and β-methylglucosides in a yield of 95 per cent of the theoretical.[5] This showed that cotton is composed entirely of anhydroglucose residues.

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[1] W. N. Haworth and E. L. Hirst, *J. Chem. Soc.*, **119** (1921), 196.

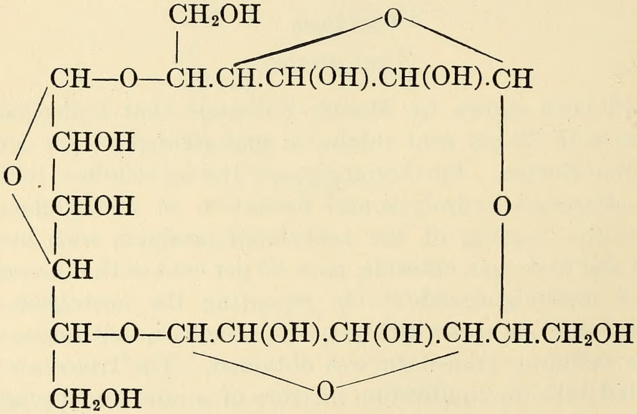
[2] H. Hibbert, *J. Ind. Eng. Chem.*, **13** (1921), 256, 334.

[3] G. W. Monier-Williams, *J. Chem. Soc.*, **119** (1921), 803.

[4] J. C. Irvine and C. W. Soutar, *J. Chem. Soc.*, **117** (1920), 1489–1500.

[5] J. C. Irvine and E. L. Hirst, *J. Chem. Soc.*, **121** (1922), 1585–1591.

It was now known that cellulose on degradation gave some cellobiose, and a nearly quantitative yield of glucose. Furthermore, the formation of 2, 3, 6-trimethylglucose showed that in a portion of the cellulose molecule positions 1 and 5 were protected from methylation, but whether all the glucose residues were alike remained unknown. This point was clarified by Irvine and Hirst[1] in a continuation of their neat research. A trimethylcellulose, which contained 43 per cent methoxyl after 20 methylations, was heated with methyl alcohol and hydrogen chloride. There was obtained 91.5 per cent of the theoretical yield of an equilibrium mixture of α- and β- 2, 3, 6-trimethylglucosides. The mixture on hydrolysis gave 86 per cent of the theoretical yield of 2,3,6-trimethylglucose. No isomeric trimethylglucose was present. This proved that all the glucose residues in cellulose have the hydroxyl groups in positions 2, 3, and 6 unsubstituted. Since the highest yield of cellobiose claimed did not exceed 60 per cent, cellulose as a matter of precaution was given the structure of a symmetrical tri-1, 5-anhydroglucose.


CH₂OH
O
CH—O—CH.CH.CH(OH).CH(OH).CH
CHOH
O
CHOH
O
CH
CH—O—CH.CH(OH).CH(OH).CH.CH.CH₂OH
CH₂OH
O

Cellulose (*Irvine*)

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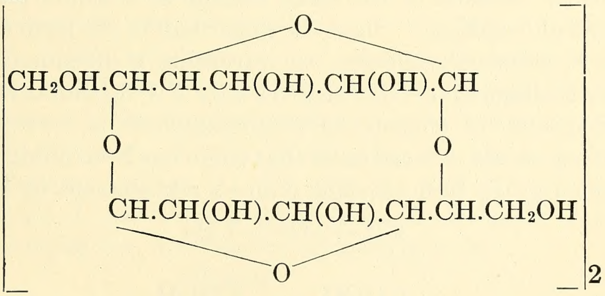
[1] J. C. Irvine and E. L. Hirst, *J. Chem. Soc.*, **123** (1923), 518–532; *J. Soc. Chem. Ind.*, **41** (1922), 362–363R; *cf. Ibid.*, **44** (1925), 242.

It is now possible to exclude most of the other structures proposed for cellulose, owing to their inability to furnish quantitative yields of 2, 3, 6-trimethylglucose.[1]

It has been shown in the chapter on the distillation of cellulose that the formation and structure of β-glucosan has little bearing on the constitution of cellulose. On treatment with chloral and sulphuric acid, α-glucosan gives parachloralose and β-glucosan gives chloralose.[2] Cellulose under the same treatment gives dichloralglucoses.[3]

Karrer[4] considered both starch and cellulose to be built up of $C_{12}H_{20}O_{10}$ units. Cellulose was looked upon as a dimeride of anhydrocellobiose, cellosan, polymerization taking place through subsidiary valencies without rupture of the oxygen bridges, the arrangement and cohesive forces being similar to those existing in a crystal.



Cellulose (*Karrer*) I

This formula was subsequently changed to (II),[5] since triacetylcellulose on heating with phosphorus pentabromide gave tri-

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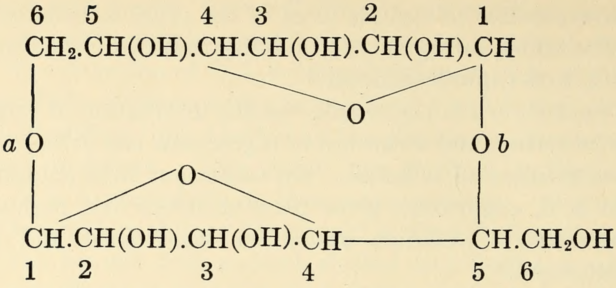
[1] L. Vignon, *Compt. rend.*, **127** (1898), 873; C. F. Cross and E. J. Bevan, *J. Chem. Soc.*, **79** (1901), 366; A. G. Green and A. G. Perkin, *J. Chem. Soc.*, **89** (1906), 811; A. G. Green, *Z. Farben-u. Textil. Chem.*, **3** (1904), 97; H. de Mosenthal, *J. Soc. Chem. Ind.*, **30** (1911), 782; K. Gebhard, *Chem. Ztg.*, **37** (1913), 663; B. Tollens, "Kohlenhydrate," Leipzig (1914), p. 564; H. Barthelemy, *Caoutchouc & gutta-percha*, **14** (1917), 9274; K. Hess, *Z. Elektrochem.*, **26** (1920), 232; *Helvetica Chim. Acta*, **3** (1920), 620; A. C. von Euler, *Chem. Ztg.*, **45** (1921), 977.

[2] A. Pictet and F. H. Reichel, *Helvetica Chim. Acta*, **6** (1923), 621–627.

[3] J. H. Ross and J. M. Payne, *J. Am. Chem. Soc.*, **45** (1923), 2363–2366.

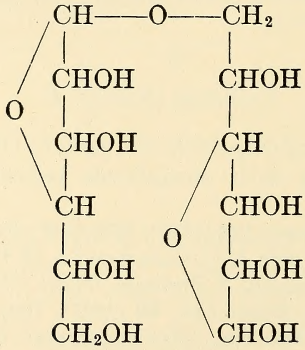
[4] P. Karrer, *Cellulosechemie*, **2** (1921), 127.

[5] P. Karrer and A. P. Smirnov, *Helvetica Chim. Acta*, **5** (1922), 187–201.



Cellulose (*Karrer*) II

aceto-1,6-dibromoglucose (m.p. 175°; $[\alpha]_D^{19^\circ} = +192^\circ$). It was shown that with pentacetylglucose the acetyl group in position 6 was not replaced by bromine under similar treatment, and that acetodibromoglucose was not obtained from cellobiose octacetate. Fission of the ether linkage at *a* would give cellobiose and at *b* maltose. Since the upper half of the formula would give 2, 3, 5-trimethylglucose, the structure is incompatible with Irvine's findings that cellulose gives only 2, 3, 6-trimethylglucose. The formation of triaceto-1,6-dibromoglucose is, however, disconcerting unless it is assumed that there has been a migration of the acetyl group from position 6 and a replacement by bromine.



Maltose[1]

This reaction would be expected from Fischer and Armstrong's[2] preparation of triaceto-1,6-dibromoglucose by the action of hydrogen bromide on glucose pentacetate. Zechmeister[1] has shown that the presence of hydrogen bromide is essential to the action of acetyl bromide on cellulose and as degradation proceeds there is a partial replacement of acetyl groups by bromine.

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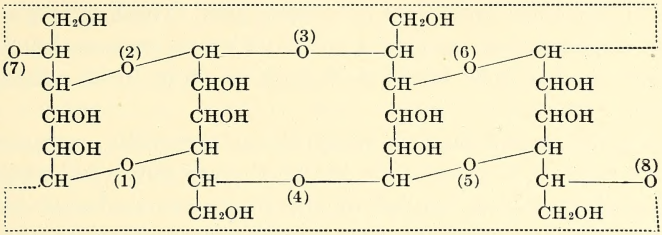
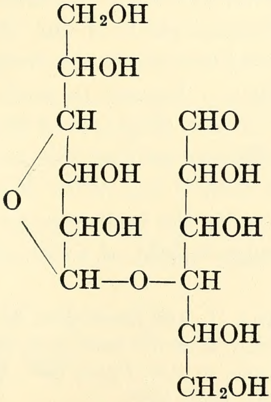
[1] W. N. Haworth and G. C. Leitch, *J. Chem. Soc.*, **115** (1919), 809.

[2] E. Fischer and E. F. Armstrong, *Ber.*, **35** (1902), 833.

A formula has been suggested by Schorger[2] in which four orthoglucosan groups are symmetrically arranged to form a parallelopiped. This polycyclic structure explains the resistance of cellulose to hydrolysis, the quantitative formation of 2,3,6-trimethylglucose, and the possibility of obtaining a quantitative yield of either cellobiose or an isomer, isocellobiose. The customary small yields of cellobiose are due to equal chances for the formation of the two disaccharides, the isomer being the more readily hydrolyzed. Fission at (1), (2), (4), (5), and (6) would give cellobiose, and at (7), (8), (1), (3), and (4) isocellobiose. Acceptance of this formula depends on the isolation of a disaccharide having the constitution of isocellobiose.





Isocellobiose

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[1] L. Zechmeister, *Ber.*, **56** (1923), 573–578.

[2] A. W. Schorger, *J. Ind. Eng. Chem.*, **16** (1924), 1274.

Some interesting experiments have been made by Hibbert[1] and his pupils leading to the synthesis of cellulose and related carbohydrates. Condensation of bromoacetaldehyde with various polyatomic alcohols yielded acetals related to the carbohydrates. The hydroxyl groups in γ,δ-positions with reference to the carbonyl group appear to be key positions in the condensation of monoses to polysaccharides. When γ,δ-dihydroxybutylmethylketone is heated with a trace of mineral acid, it undergoes a cyclic acetal condensation to give a resin which is presumably a trimeride. Inulin may be formed from fructose in an analogous way.[2]

The polysaccharides are probably heterocyclic compounds, and information is greatly needed on the stability of the higher-membered rings. A study[3] of the formation and stability of cyclic acetals has shown that six-membered rings are more stable and more easily formed than the five or seven. The closed spiral ring structure proposed to account for the polymerization of cellulose lacks symmetry, and the bridge linkage would appear to be particularly susceptible to fission.

Aside from the probable mode of linkage nothing is known of the order of arrangement and number of orthoglucosan groups forming the cellulose molecule. The number was formerly considered to be very high, the molecular weight having been determined by ordinary methods which are not applicable to colloids. Geinsperger,[4] from a determination of the chlorine content of acetochlorocellulose, arrived at a molecular weight of 5508, which is equivalent to $(C_6H_{10}O_5)_{34}$. Joyner[5] in studying the viscosity of cellulose solutions found that 16 grams of oxygen reacted with about 2500 grams of cellulose, so that the molecular weight of cellulose must be at least 2500 if one atom of oxygen reacts with one molecule of cellulose. By the boiling-point method, cellulose acetate[6] showed a molecular weight of 6480, which is equivalent to $(C_6H_{10}O_5)_{40}$, and nitrocellulose,[1] $(C_6H_{10}O_5)_{12}$. High variable molecular weights were obtained by Hess,[2] using various cellulose derivatives. Trimethylcellulose A, *e.g.*, in aqueous solution, gave molecular weights varying from 1400 to 8700.

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[1] H. Hibbert and H. S. Hill, *J. Am. Chem. Soc.*, **45** (1923), 734–751.

[2] H. Hibbert and J. A. Timm, *J. Am. Chem. Soc.*, **45** (1923), 2433–2439.

[3] H. S. Hill and H. Hibbert, *J. Am. Chem. Soc.*, **45** (1923), 3117–3124; 3124–3132; *cf. Ibid.*, **46** (1924), 1281, 1283.

[4] E. Geinsperger, *Monatsh.*, **26** (1905), 1467.

[5] R. A. Joyner, *J. Chem. Soc.*, **121** (1922), 2395.

[6] A. Nastjukoff, *Ber.*, **33** (1900), 2241.

Our usual conception of a molecule has undergone great change through Werner's[3] theory of primary and secondary valencies, and the use of X-ray spectrograms. According to Langmuir,[4] any solid or liquid body must be considered as a single large molecule consisting of atoms held together by chemical forces. Cohesion, adsorption, and such changes of state as evaporation, condensation, solution, and crystallization are chemical phenomena. Harrison[5] has suggested that the entire cellulose fiber may be regarded as the molecule.

The use of the terms "polymerization" and "depolymerization" in connection with cellulose should be discontinued, as they have a meaning in organic chemistry not applicable to colloids. Harries[6] has suggested that they be replaced by aggregation and disaggregation. The supposed polymerization of drying oils has been shown to be colloidal gelation. Molecular-weight determinations show that only a trace of condensation has taken place in the thickened oil.[7] The term "association"[8] is objectionable, owing to its established use to describe the weak union of two or more molecules of a substance, as shown by molecular-weight determinations, by mere solution in a solvent.

Our present conception of the size of the cellulose molecule varies from a large indefinite number[9] of glucose residues held together by cellobiose linkages to a small definite number. Wise[1] pictures cellulose as an aggregate of a large number of small units held together by secondary valencies, no suggestion being made regarding the size of these units. Zwickker[2] represents the molecule as composed of nine glucose residues arranged to form the edges of a triangular prism. According to Karrer,[3] cellulose is a dimeride of anhydrocellobiose units held together by subsidiary valencies.

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[1] G. Bumcke and R. Wolffenstein, *Ber.*, **32** (1899), 2495, 2506.

[2] K. Hess, *Ann.*, **435** (1924), 1–144.

[3] A. Werner, "Neure Anschauungen auf dem Gebiete der anorganischen Chemie," Braunschweig (1905); F. Henrich, "Theories of Organic Chemistry," N. Y. (1922).

[4] I. Langmuir, *J. Am. Chem. Soc.*, **38** (1916), 2221–2295.

[5] W. Harrison, *Second Rept. Colloid Chem. Brit. Assn. Adv. Science* (1921), p. 55.

[6] C. Harries, *Ber.*, **56** (1923), 1048.

[7] H. Wolff, *Z. angew. Chem.*, **37** (1924), 729; R. S. Morrell, *J. Soc. Chem. Ind.*, **43** (1924), 362T.

[8] H. Hess, *l.c.*, 104.

[9] H. Hibbert, *J. Ind. Eng. Chem.*, **13** (1921), 256; J. C. Irvine and E. L. Hirst, *J. Chem. Soc.*, **123** (1923), 525; A. C. von Euler, *Chem. Ztg.*, **45** (1921), 977, 998.

Hess[4] holds the extreme view that cellulose consists of $C_6H_{10}O_5$ units held together by association. Through a study of the optical rotation of cuprammonium solutions of cellulose of varying composition, it was found that these solutions obeyed the law of mass action, a condition explainable only on the assumption that the chemical unit in cellulose is $C_6H_{10}O_5$. All forms of cellulose free from impurities reached almost instantly a maximum rotation at the point corresponding to 1 Cu:1 $C_6H_{10}O_5$. This indicates that no ether linkages were ruptured, since the hydrolysis of carbohydrates is a time reaction. Saponification of cellulose acetate A gave cellulose A that also behaved like pure cotton cellulose in cuprammonium solution. It would seem hazardous to draw such sweeping conclusions from the behavior of a reagent having so special an action on carbohydrates as cuprammonium. Grossmann[5] found that in alkaline copper solutions the optical rotation of sugars was greatly changed and frequently reversed; thus for dextrose $[\alpha]_{hb} = +78°$ became $-375°$, while fructose showed $+1423°$.

Hess was also able to synthesize a derivative of cellobiose in the following way: Treatment of cellulose acetate A with a mixture of acetyl bromide and hydrogen bromide at $-15°$ gave a new tetracetylbromoglucose, m.p. 60 to 70°; $[\alpha]_D^{24°} = ca. +80°$. On allowing an ether-chloroform solution of this tetracetylbromoglucose to stand in moist air at 2 to 3° for several days there was obtained celloglucosan, $C_6H_{10}O_5.H_2O$, m.p. 107 to 109°; $[\alpha]_D = +89.3°$ (in water). The tribenzoate of celloglucosan on treatment with acetyl bromide and hydrogen bromide gave heptacetylbromocellobiose, which was obtained directly from cellulose acetate A by the same treatment. Hess concludes that the anhydrocellobiose group does not necessarily exist in the cellulose molecule but may be formed by a secondary reaction. This possibility is rather remote in spite of the fact that isomaltose[1] and apparently a trisaccharide[2] have been obtained by the action of hydrochloric acid on glucose. The bacterial degradation of cellulose through cellobiose,[3] under conditions precluding the likelihood of enzymatic synthesis, is strong evidence that the cellobiose linkage preexists in cellulose. The resistance of cellulose to hydrolysis renders it difficult to accept a $C_6H_{10}O_5$ entity for cellulose, since all the anhydroglucoses so far obtained are readily hydrolyzable. To accept Hess' view, it would be necessary to assume from available experimental evidence that the secondary valencies in cellulose are stronger then the primary valencies, which is turning the tables.

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[1] L. E. Wise, *J. Ind. Eng. Chem.*, **15** (1923), 711.

[2] J. J. Zwickker, *Rec. trav. chim.*, **41** (1922), 49.

[3] P. Karrer, *Cellulosechemie*, **2** (1921), 127.

[4] K. Hess *et al.*, *Ann.*, **435** (1923), 1–144; *Z. angew. Chem.*, **34** (1924), 993.

[5] H. Grossmann, *Z. Ver. deut., Zücker-Ind.*, **56** (1906), 1024.

Some interesting results on the structure of cellulose have been obtained by the use of X-rays, but the data are too meager to be accepted with finality. All methods depend on the diffraction of the X-ray waves by the planes of atoms, which have a space lattice within the crystal. Only crystalline substances diffract X-rays. The original method of Laue depends on passing a pencil of X-rays through a thin oriented section of a crystal, a point diagram being obtained. In the spectroscopic method developed by the Braggs the X-rays are reflected from atomic planes parallel to the smooth surface of an oriented crystal. The method of most general application consists in subjecting a narrow tube, containing the finely powdered substance to be examined, to a ribbon-like beam of X-rays. With a finely powdered crystalline substance, the atomic planes are oriented in all directions, but only those planes that chance to lie in the proper direction are effective. The diffracted rays are registered on a film as a series of parallel lines of varying intensity and characteristic pattern (Fig. 4).

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[1] E. Fischer, *Ber.*, **23** (1890), 3687.

[2] E. Grimaux and L. Lefèvre, *Compt. rend.*, **103** (1886), 146.

[3] H. Pringsheim, *Z. physiol. Chem.*, **78** (1912), 266.

The X-ray examination of cellulose indicates that it is crystalline (Fig. 5). Cotton, ramie, and wood pulp that had been reduced

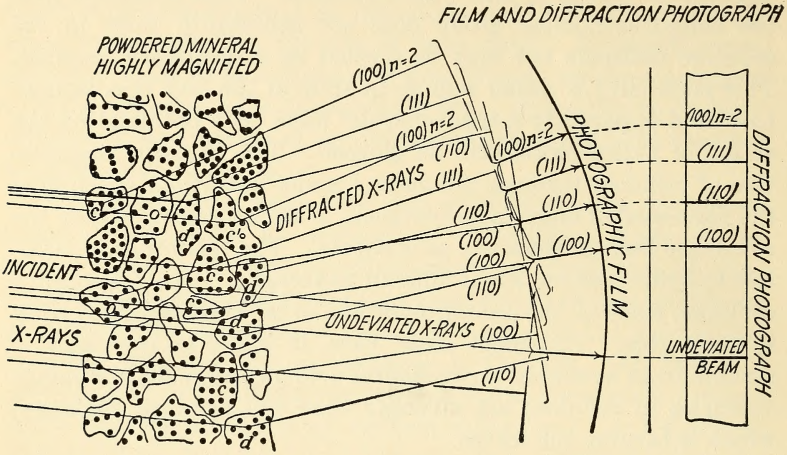

Fig. 4.—Idealized representation of the diffraction of a monochromatic beam of X-rays from a crystalline powder. Atomic planes are indicated by dots. (*After Kerr.*)

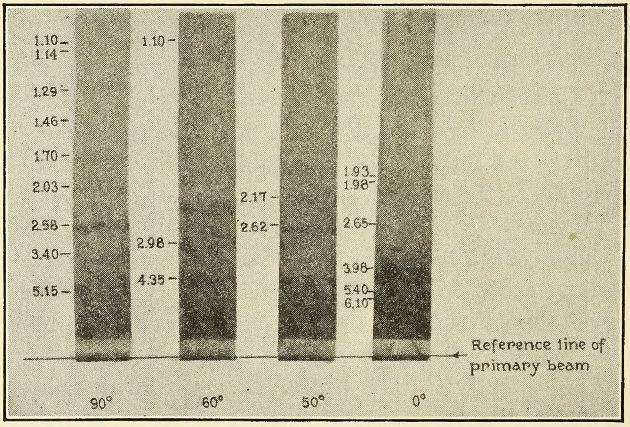

Fig. 5.—Spectrograms of bundles of ramie fibers (*Boehmeria nivea*) taken at various angles with reference to the long axes of the fibers. Figures in the vertical columns represent the interplanar spacings in Å.U. (*After Sponsler.*)

to a fine state of division by exposure to the vapors of hydrochloric acid gave identical patterns; hence their crystalline forms were identical.[1] The cellulose spectrogram indicates that the crystals are arranged symmetrically with respect to the axis, groups of four $C_6H_{10}O_5$ units, arranged in the form of a parallelopiped, being regularly repeated.[2] Gonell[3] concludes from the structure of the individual points in the patterns of various celluloses that more than one crystalline substance must be present. The various artificial silks, with the exception of cellulose acetate, show a crystalline structure.[4] The difference between the diagrams appears in the arrangement of the crystallites with respect to the axis of the fiber. Irregular arrangement produces a ring diagram and a regular arrangement a point diagram. The artificial silks give an intermediate pattern. Cotton treated with a mercerizing solution of sodium hydroxide and washed without tension gives a ring diagram; if washed under tension the fiber shows a point diagram.[5] Tunicin gives the same diagram as ramie cellulose; lichenin a different one.[6]

Careful investigations on the X-ray diffraction patterns of starch and cellulose have been made by Sponsler.[7] His latest values for the interplanar spacings in plant fibers are given below.[8] The conclusion was recently reached by Sponsler[9] that the

INTERPLANAR SPACINGS IN PLANT FIBERS

Å.U.	Å.U.
6.10	2.62
5.40	2.58
3.98	2.17
3.40	2.03
3.20	1.11

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[1] R. O. Herzog and W. Jancke, *Z. Physik.*, **3** (1920), 196–198; *Ber.*, **53** (1920), 2162–2164; R. O. Herzog, W. Jancke, and M. Polanyi, *Z. Physik.*, **3** (1920), 343–348.

[2] R. O. Herzog, *Cellulosechemie*, **2** (1921), 101–102; R. O. Herzog and W. Jancke, *Umschau*, **25** (1921), 53–54.

[3] H. W. Gonell, *Z. Physik.*, **25** (1924), 118–120.

[4] R. O. Herzog and H. W. Gonell, *Kolloid-Z.*, **35** (1924), 201–202.

[5] R. O. Herzog and G. Londberg, *Ber.*, **57** (1924), 329.

[6] R. O. Herzog and H. W. Gonell, *Z. physiol. Chem.*, **141** (1924), 63–67.

[7] O. L. Sponsler, *Am. J. Botany*, **9** (1922), 471–492; *J. Gen. Physiol.*, **5** (1923), 757–776; *Ibid.*, **9** (1925), 221–233; *Science*, **62** (1925), 547–548.

[8] O. L. Sponsler, *Nature*, **116** (1925), 243.

[9] Private communication.

elementary cell has the dimensions 5.40 × 6.10 × 10.30 Å.U., which is equal in volume to two $C_6H_{10}O_5$ groups. It appears to be questionable whether the diffraction patterns of plant materials are not due to the uniform arrangement with which the units are deposited during growth, rather than to a structure which is reproducible *in vitro* and crystalline in the usually accepted sense.

Optical Rotation.—Solutions of cellulose in concentrated sulphuric or hydrochloric acid,[1] and a mixture of zinc chloride and hydrochloric acid,[2] are optically inactive until hydrolysis takes place. Béchamp[3] found that cellulose dissolved in hydrochloric acid of a concentration of 39.8 per cent remained inactive for 6 hours. Willstätter and Zechmeister,[4] using a stronger acid, found optical activity after one hour. A 1 per cent solution of viscose appeared to be weakly dextro-rotatory, but difficulty in preparing a clear solution made the readings uncertain.[5]

A cuprammonium solution of cellulose in which the copper had been displaced with zinc gave a colorless solution inactive towards polarized light.[6] Lévallois[7] found that a cuprammonium solution of cellulose was optically active, a 1 per cent solution showing a rotation of approximately $-20°$ in a 200-millimeter tube. Cotton, linen, hemp, and Girard's hydrocellulose gave the same rotation under similar conditions. The rotation was not constant, but varied with the concentration of the cellulose and the ratio of copper to cellulose. The optical activity was attributed by Béchamp[8] to the cuprammonium itself, the cellulose merely augmenting the rotation as in the case of boric acid and tartaric acid. These contentions were refuted by Lévallois.[9]

The optical activity of curpammonium solutions of cellulose has been confirmed by Hess and Messmer.[10] The ammonia remaining constant, the optical activity decreased with the decrease in concentration of both copper and cellulose. The specific rotation, $[\alpha]$ = *ca.* $-950°$ to $-1000°$, is in agreement with the value found by Lévallois. Ethylcellulose dissolved in esters, viscose, and gelatinized cellulose in neutral salt solutions were optically inactive.[1] Cellulose represents a case of latent asymmetry, the cuprammonium behaving like boric acid in the case of mannitol. The cuprammonium forms a complex with the cellulose through a diversion of the subsidiary valencies holding the cellulose groups together. This complex, to which the optical activity is due, may be represented by $[C_6H_7O_5Cu]_2[Cu(NH_3)_4]$, in which one atom of copper is equivalent to one $C_6H_{10}O_5$ residue.[2]

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[1] A. Béchamp, *Compt. rend.*, **42** (1856), 1213.

[2] J. König and F. Hühn, "Bestimmung der Zellulose in Holzarten und Gespinstfasern" (1912), p. 54.

[3] A. Béchamp, *Compt. rend.*, **100** (1885), 370.

[4] R. Willstätter and L. Zechmeister, *Ber.*, **46** (1913), 2404.

[5] L. Vignon, *Bull. soc. chim.*, [3] **31** (1904), 107.

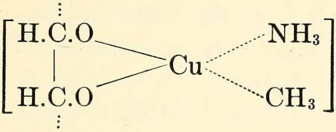
[6] E. Mulder, *Jahresb. Chemie*, (1863), 566.

[7] A. Lévallois, *Compt. rend.*, **98** (1884), 732–735.

[8] A. Béchamp, *Compt. rend.*, **99** (1884), 1027; **100** (1885), 279, 368.

[9] A. Lévallois, *Compt. rend.*, **99** (1884), 1122; **100** (1885), 456.

[10] K. Hess, E. Messmer, and E. Jagla, *Ber.*, **55** (1922), 2432.



[1] K. Hess and E. Messmer, *Ber.*, **54** (1921), 834–841.

[2] K. Hess and E. Messmer, *Ann.*, **435** (1923), 7.

CHAPTER VII

GELATINIZED CELLULOSE

Gelatinized cellulose, as the name implies, refers to cellulose having a swollen, gelatinous appearance. It may be opaque, translucent, or transparent. When the fibrous structure is wholly or largely destroyed, it forms a dense, horny product on being dried *en masse*. Ultimate analysis shows it to be identical with normal cellulose. In contrast with the latter, it shows increased hygroscopicity, solubility in cellulose solvents, ease of hydrolysis, and adsorption of dyes and cold Fehling's solution. In general also, it is more readily esterified. The greater reactivity of gelatinized cellulose may be referred in most cases to a greater surface exposure and not to a chemical change in the cellulose.

The older term "hydrated" cellulose was based on the erroneous belief that mercerization was accompanied by the addition of a molecule of water. Mercerized is not suitably descriptive, since in the strictest sense this refers to the technical operation of treating a cellulose fiber with caustic soda and stretching to produce a luster. A similar effect can be obtained with acids and salts. Schwalbe[1] has introduced the name "swollen" cellulose. This is not sufficiently definitive, since a cotton hair will increase 40 per cent in cross-sectional area by merely wetting with water. No name so far proposed is, however, entirely free from criticism.

Gelatinized cellulose may be produced through the following agencies: (1) mechanical comminution and pressure in the presence of water; (2) salts; (3) bases; (4) acids; and (5) regeneration from esters.

Gelatinized cellulose differs from hydrocellulose in having a lower copper number and a higher percentage of hygroscopic moisture.[1] The figures for various gelatinized celluloses are given below.

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[1] C. G. Schwalbe, "Ullmann's Enzyklopädie Tech. Chemie," **3** (1916), 333.

Substance	Hygroscopic moisture, per cent	Copper number before hydrolysis	Copper number after hydrolysis	Difference
Cotton wool	6.1	1.1	3.3	2.2
Cotton wool mercerized with:				
8 per cent NaOH	7.7	0.9	3.2	2.3
16 per cent NaOH	10.7	1.3	5.0	3.7
24 per cent NaOH	11.3	1.2	6.1	4.9
40 per cent NaOH	12.1	1.9	6.6	4.7
Glanzstoff silk	9.8	1.5	12.8	11.3
Viscose silk A	10.7	1.9	14.0	12.1
Viscose silk B	10.2	3.0	14.5	11.5
Viscose silk C	11.0	2.9	16.6	13.7
Chardonnet silk	11.4	4.1	17.7	13.6
Girard's hydrocellulose	3.6	5.7	6.6	0.9
Mitscherlich wood pulp, unbleached	....	2.4	4.4	0.9
Ritter-Kellner wood pulp	....	2.8	3.5	2.7

Coloration with Iodine.—Iodine reagents stain gelatinized cellulose, the color and its stability being dependent on the degree of gelatinization. Barreswil[2] observed that cellulose swollen by caustic soda and potash is colored blue by iodine. Lange[3] found that when ordinary cotton was stained with zinc chloriodine, the color was rapidly removed by washing with water, while under the same conditions mercerized cotton remained blue for a considerable time. It has been stated[4] that gelatinized cellulose generally reacts with iodine in aqueous solution to give a blue color, though Hübner[5] was unable to obtain this color with mercerized cotton.

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[1] C. G. Schwalbe, *Z. angew. Chem.*, **22** (1909); 197; *cf. Ibid.*, **20** (1907), 2166.

[2] C. Barreswil, *J. pharm. chim.*, **21** (1852), 205.

[3] H. Lange, *Färber-Ztg.*, **14** (1903), 365.

[4] C. F. Cross and E. J. Bevan, "Cellulose," (1895), p. 7.

[5] J. Hübner, *J. Soc. Chem. Ind.*, **27** (1908) 105.

A qualitative test of the degree of gelatinization may be obtained by staining the cellulose blue with zinc chloriodine and observing the rapidity with which the color is removed by washing with water.[1] Iodine-potassium iodide solution may be used, but it is less satisfactory. Celluloses having a high degree of gelatinization, such as mercerized cotton, parchment paper, and viscose silk, retain the blue color for a considerable time. The color disappears from Pauly silk (cuprammonium process) very rapidly. While cellulose gelatinized with strong chemical reagents may retain the blue color under washing for an hour, mechanically gelatinized cellulose loses its color almost immediately.[2]

The best solution for distinguishing between ordinary cotton and cotton mercerized with caustic soda is prepared as follows:[3]

A. Two-hundred and eighty grams of zinc chloride made up to 300 cubic centimeters with water.

B. One gram of iodine and 20 grams of potassium iodide in 100 cubic centimeters of water.

C. To 20 cubic centimeters of A are added 4 drops of B. The resulting solution C stains mercerized cotton a very dark, reddish-navy-blue shade, while ordinary cotton is faintly tinted reddish. Cotton that has been treated with saliva or mercerized with sulphuric, nitric, and syrupy phosphoric acids, saturated solutions of zinc chloride and sodium sulphide, and barium mercuric iodide also give the characteristic blue color. Cotton treated with hydrochloric acid and saturated solutions of potassium mercuric iodide, or potassium iodide, behaves like ordinary cotton.

Hygroscopic and Colloid Water.—Cross and Bevan[4] considered as hydrated those forms of cellulose containing water of constitution, but not of hydrolysis, as in the case of hydrocellulose. Hygroscopic moisture, the amount of which is dependent on atmospheric conditions, is removed at 100°, while water of hydration passes off at appreciably higher temperatures. To designate the various forms of water, "aq" was proposed for that driven off at 100°, "Aq" for that evolved on further heating up to 150°, and H_2O for water actually retained through hydrolysis.[1] The evolution of water from gelatinized cellulose at various temperatures has been compared to the behavior of inorganic substances containing water of crystallization.[2]

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[1] C. G. Schwalbe, *Ber.*, **40** (1907) 4525: *Z. angew. Chem.*, **20** (1907) 2169.

[2] C. G. Schwalbe, *Z. angew. Chem.*, **32** (1919) 356.

[3] J. Hübner, *J. Soc. Chem. Ind.*, **27** (1908), 107.

[4] C. F. Cross and E. J. Bevan, "Researches" (1901), p. 27; "Cellulose" (1905), pp. 23, 29.

Higgins[3] found that the hygroscopicity of mercerized cotton increased with the concentration of the sodium hydroxide employed.

	NaOH, specific gravity	Moisture, per cent
Ordinary cotton	0	6.2
Mercerized with	1.05	6.37
Mercerized with	1.10	6.68
Mercerized with	1.15	8.40
Mercerized with	1.20	9.41
Mercerized with	1.25	9.43
Mercerized with	1.30	9.57
Mercerized with	1.35	9.69

Viscose in an atmosphere saturated with moisture at normal temperature will take up about 30 per cent of its original weight of water.[4] It is stated by Beadle[5] that cotton or viscose when finely ground is less hygroscopic than large pieces. Normal cotton contains 7 per cent of moisture in comparison with 4 per cent for the ground material. This is explained on the theory that hygroscopicity depends on internal stresses in the cellulose and that comminution reduces them. It has been shown recently that cellulose undergoes decided changes even with careful dry grinding.[6] The individual particles swell instantly and assume the shape of spheres on contact with water. The cellulose becomes partially soluble in water, and shows a greater reduction of Fehling's solution and ease of hydrolysis as grinding progresses.

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[1] C. F. Cross and E. J. Bevan, *Chem. Ztg.*, **33** (1909), 368.

[2] C. G. Schwalbe, *Z. angew. Chem.*, **20** (1907), 2167; C. F. Cross, *Ber.*, **44** (1911), 153.

[3] S. H. Higgins, *J. Soc. Chem. Ind.*, **28** (1909), 188.

[4] H. S. Mork, *J. Franklin Inst.*, **184** (1917), 353.

[5] C. Beadle, *J. Franklin Inst.*, **143** (1897), 12.

[6] H. Wislicenus and W. Gierisch, *Kolloid Z.*, **34** (1924), 169.

The hygroscopic water, according to Schwalbe,[1] could be determined by heating at 100 to 105°. Distillation with kerosene gave the total water from which the hygroscopic water was subtracted to obtain the water of hydration.

	WATER OF HYDRATION, PER CENT
Cotton cloth	0.23
Cotton, beaten to a pulp	1.56
Cotton, mercerized and beaten to a pulp	6.31

This distinction is considered invalid by Ost and Westhoff,[2] since small progressive losses[3] of water are obtained by raising the temperature from 100 to 130°. In no case are fixed points obtained. Gelatinized cellulose contains more hygroscopic moisture than normal cellulose or hydrocellulose, and this can be determined accurately by gradually raising the temperature of the material, preferably in an atmosphere of dry hydrogen or carbon dioxide, to 125°. The hygroscopic moisture of mercerized cotton and hydrocellulose, determined at 130°, was 10.05 and 4.73 per cent, respectively. Distillation with xylol gave no more water than drying at 120 to 125°. Mercerized cotton and viscose dried at the latter temperatures had exactly the same ultimate composition as normal cellulose. These conclusions have been vigorously disputed.[4]

Miller[5] had shown that a cellulose hydrate did not exist. Ordinary cellulose contained 7.12 per cent and mercerized cellulose 10.0 per cent of water at a temperature of 21.5 to 22.5°. When the mercerized cellulose was exposed to anhydrous calcium chloride, the water evaporated at a rate corresponding to an adsorbed and not a chemically combined substance.

No satisfactory evidence has yet been presented to show that mercerized cellulose differs in chemical constitution or composition from normal cellulose, though various physical measurements show a difference. Ost[1] found that the viscosities of cuprammonium solutions of mercerized and untreated cotton were practically identical and concluded that no chemical change accompanied mercerization. Nakano,[2] however, found that cuprammonium solutions of mercerized cotton showed a decided decrease in viscosity. The cotton, 10 grams, was mercerized by treatment with 200 cubic centimeters of sodium hydroxide for 24 hours. The relative viscosities of the cuprammonium solutions of cotton mercerized with various strengths of sodium hydroxide were:

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[1] C. G. SCHWALBE, *Z. angew. Chem.*, **20** (1907), 2166.

[2] H. OST and F. WESTHOFF, *Chem. Ztg.*, **33** (1909), 197; *Ann.*, **382** (1911), 354.

[3] *cf.* C. F. CROSS and E. J. BEVAN, "Cellulose" (1895), p. 4.

[4] C. F. CROSS and E. J. BEVAN, "Researches" (1905–1910), pp. 36–38.

[5] O. MILLER, *Ber.*, **43** (1910), 3430; **44** (1911), 728; *cf.* C. G. SCHWALBE, *Ibid.*, **44** (1911), 151; C. F. CROSS, *Ibid.*, **44** (1911), 153.

NaOH, per cent	Viscosity	NaOH, per cent	Viscosity
0	4.22	17	3.03
11	3.59	20	2.01

It would seem that the act of dissolving in cuprammonium solution might mask mercerization or produce effects similar to it.

Gelatinized cellulose in many ways behaves as a hydrophilic colloid. It should, accordingly, be possible to obtain definite information as to the presence of "bound" water by applying the method of Newton and Gortner[3] for determining the hydrophilic colloid content of expressed plant fluids. The freezing-point depression, Δ, of the liquid is first obtained. The water content is then determined by any convenient method. To a weighed portion of the liquid, sufficient sucrose is added to make an exactly molar solution in the total water that is present, and a new freezing-point depression, Δa, is then taken. In case no bound water occurs, the second freezing-point depression will be 2.085° lower than Δ. When hydrophilic colloids are present there should be a depression greater than 2.085°, since some of the water, being bound by the colloids, is not free to dissolve the sugar.

Theories of Gelatinization.—Gelatinization is here used in a narrower sense than hydration. The subject of hydration in the cacti has been extensively investigated by MacDougal.[1] He states:

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[1] H. Ost, *Z. angew. Chem.*, **24** (1911), 1892.

[2] M. Nakano, C. A., **16** (1922), 2405.

[3] R. Newton and R. A. Gortner, *Botan. Gaz.*, **74** (1922), 442–446.

> The source of energy in growth and swelling is the unsatisfied attraction of molecules, or particles, or ions bearing an electrical charge. Substances made up in this manner may unite with definite proportions of water which become part of a symmetrical chemical structure, the union being known in classical chemistry as hydration. In addition, however, it is known that such particles may also adsorb and hold in combination additional molecules of water, an action especially characteristic of swelling in colloids, and the term hydration is used in the present work to include the entire range of action.

According to Ostwald,[2] peat may hold water in five forms: (1) water of occlusion, held in spaces 1 millimeter and more in diameter; (2) capillary water; (3) colloidally bound water; (4) osmotically bound water; (5) chemically combined water, as in hydrocellulose, or water of crystallization, as in copper sulphate. The term "hydration" should be, accordingly, confined to the broad phenomena of the taking up of water in all its forms.

It has long been realized that the gel state of cellulose is of great importance in the plant kingdom. The cellulose in young wood in comparison with old is much less resistant to chemical reagents.[3] The amount of cellulose isolatable from green fodder plants is increased by a preliminary dehydration with alcohol.[4]

The phenomenon of "hydration" has been described[5] as a condition of intermolecular distention whereby the surface reactions are largely increased and the adsorption property correspondingly developed.

The cause of gelatinization is not at all clear. Some of the theories that have been advanced to account for the phenomenon of the swelling of colloids, that have a bearing on the swelling of cellulose are:

1. The capillary theory, in which it is assumed that swelling takes place by the passage of the liquid through small pores, the

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[1] D. T. MacDougal, "Hydration and Growth," *Carnegie Inst. Pub.*, **297**, Washington (1920).

[2] W. Ostwald, *Kolloid Z.*, **29** (1921), 318.

[3] C. G. Schwalbe, *Z. angew. Chem.*, **22** (1909), 197.

[4] C. F. Cross and E. J. Bevan, "Cellulose" (1895), p. 7.

[5] J. F. Briggs, *Ann. Rep. Soc. Chem. Ind.*, **2** (1917), 128.

impelling force being the difference in surface tension between solvent and solution.

2. The osmotic theory,[1] in which liquids pass into the substance, the swelling being due to the difference in osmotic pressure between the external and internal solutions. Bartell and Sims[2] assume that in the swelling of a gel the latter consists of a framework of cells and that some unit of this framework functions as a permeable membrane. Swelling is due to imbibition—a process which is not well understood and which may be due to capillary action or to intermolecular reactions—together with the operation of effects that produce anomalous osmosis. The curves for swelling and osmosis show a close parallel. When a gel swollen in pure water is placed in a solution of an electrolyte an abnormal swelling effect would be due to negative osmotic action, and shrinking to an abnormally positive osmotic action.

3. In the solid-solution theory of Katz,[3] colloidal substances capable of swelling are highly viscous liquids. The addition of a miscible liquid to such substances forms a solid solution.

4. The electrostatic repulsion theory.[4] A gel consists of a sponge-like structure with many minute pockets filled with water. On the addition of acid or alkali, H or OH ions, respectively, are adsorbed on the surface of these pockets. The colloid particles become charged with electricity of the same sign. Owing to electrostatic repulsion, increase in size by imbibition of solution takes place. The addition of a neutral salt produces a decrease in swelling, due to neutralization of the original electrostatic repulsion.

The cellulose fiber, according to Bovard,[5] consists of a sponge-like structure of colloid particles, strongly charged negatively, and held together by capillary attraction. This structure has the power of adsorbing hydroxyl ions and, since the latter are more abundant in an alkaline medium, gelatinization takes place most rapidly in a basic solution. The positive sodium or hydrogen ions, *e.g.*, are drawn towards the cellulose particles by reason of the electrostatic attraction of the positive and negative charges and, since they have like charges, they tend to repel one another. It is this pulling force or tendency to expand that causes the cellulose to swell with the simultaneous absorption of water. A similar theory has been developed by Gesell and Minor.[1]

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[1] W. Pfeffer, "Osmotische Untersuchungen," Leipzig (1877), 236 pp. C. P. Smith, *J. Am. Chem. Soc.*, **43** (1921), 1350.

[2] F. E. Bartell and L. B. Sims, *J. Am. Chem. Soc.*, **44** (1922), 289: F. E. Bartell, "Colloid Symposium Monograph," Madison, Wis. (1923), 120.

[3] J. R. Katz, *Z. physiol. Chem.*, **96** (1916), 255; *Kolloidchem. Beihefte*, **9** (1917), 182.

[4] R. C. Tolman and A. E. Stearn, *J. Am. Chem. Soc.*, **40** (1918), 264.

[5] W. M. Bovard, *Paper*, **22**, 3 (1918), 11–16.

The adsorption of hydroxyl ions by cellulose, which has a marked residual valence, is greatly aided by mechanical treatment, such as beating in the presence of water.[2] The hydroxyl ions hydrolyze the cellulose molecule with increasing velocity into a series of products, the first being insoluble and mucilaginous, the later ones soluble dextrins or acids. The formation of cellulose "mucilage" is a hydrolytic reaction and must be distinguished from gelatinization, even though the two reactions may occur simultaneously. Knoevenagel[3] attributes the formation of cellulose mucilage to the setting free of residual affinities by disintegration of the large cellulose molecule. Both acids and alkalis may set free residual affinities, thus making the modified cellulose more reactive.

5. The diffusion-pressure theory of Proctor and Wilson.[4] The force producing the swelling is due to the diffusion of the necessary excess concentration of diffusible ions of the gel phase over that of the external solution. Gelatin behaves as an amphoteric colloid and forms highly ionized salts with acids and bases. The non-colloid ion on diffusing out exerts a pull that swells the gel.

Of the ionized gelatin chloride the chloride ions remain in the solution in the interstices while their corresponding gelatin cations form part of the network and are not in solution in the same sense as the chloride ions. Because these chloride ions are balanced only by the positive electrical charges on the gelatin network, there results an unequal distribution of all ions between the external solution and that absorbed by the gelatin such that the total concentration of ions is always greater in the jelly than in the external solution. In tending to diffuse into the external solution the anions of the protein salt exert a pull upon the cations forming part of the gelatin network, causing an increase in volume of the jelly directly proportional to the excess of concentration of diffusible ions of the jelly over that of the external solution.[1]

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[1] W. H. Gesell and J. E. Minor, *Paper*, **24**, 12 (1919), 15–19.

[2] J. E. Minor, *J. Ind. Eng. Chem.*, **13** (1921), 131.

[3] E. Knoevenagel and H. Busch, *Cellulosechemie*, **3** (1922), 43.

[4] H. R. Procter and J. A. Wilson, *J. Chem. Soc.*, **109** (1916), 307; J. A. and W. H. Wilson, *J. Am. Chem. Soc.*, **40** (1918), 264.

Donnan[2] in his theory of membrane equilibrium was the first to stress the importance of the unequal distribution of diffusible crystalloidal ions on the swelling of colloids. His theory has been of the highest importance in explaining the chemistry of tanning, and it has been applied to the swelling of cellulose.[3] It is improbable that any one theory can be made to fit all cases. The swelling of rubber in benzene might be explained on the solid-solution theory, while the other theories would fall down.

It appears that ions are hydrated and that they carry water molecules with them. Hence, if the ions are adsorbed on the surface of the colloid particle, there is a concentration of water about the particle.[4]

According to Fischer,[5] hydration is a change by which the colloid enters into physicochemical combination with water. Solution, on the other hand, is the expression of the degree of dispersion of the colloid. The two are antagonistic, for finely dispersed colloid particles are incapable of binding as much water as coarse.

The dilution at which some substances will form a gel is amazing. The glucoside apiin from parsley is stated not to lose its ability to gelatinize until 8500 parts of water have been added.[6] It is generally accepted that in gel formation the molecules unite to form interlacing filaments. In this way water or other liquid may be held by capillarity in addition to adsorption. A hot aqueous solution of caffeine on cooling forms a false gel of interlacing crystalline needles. Dibenzoylcystine[1] forms a solid transparent gel containing 99.8 per cent of water. It has a fibrillar structure made up of exceedingly minute crystals.

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[1] J. A. Wilson, "Colloid Symposium Monograph," Madison, Wis. (1923), p. 226.

[2] F. G. Donnan, *Z. Elektrochem.*, **17** (1911), 572.

[3] J. E. Minor, *Paper Trade J.*, **76**, 23 (1923), 55–59.

[4] T. Svedberg, "Colloid Chemistry" (1924), p. 178.

[5] M. H. Fischer, *Kolloid Z.*, **17** (1915), 2.

[6] E. von Gerichten, *Ber.*, **9** (1876), 1122.

A solution of viscose on exposure to the air forms a network of interlacing cellulose filaments.[2] This may explain why a cellulose coagulum from viscose, containing 85 per cent of water, when dehydrated under high pressure, instead of forming a solid sheet, sometimes shows a laminated structure.[3]

Dyeing Properties.—Higgins[4] found a direct relation between the hygroscopicity of cotton and the adsorption of dyestuffs. Mercerized cotton does not dye to as full a shade after drying as before, the wet and dried fibers taking up 1.74 and 1.16 per cent, respectively, of benzopurpurin.[5] The change is apparently permanent, as it is not restored by exposure to air or prolonged steeping in water. Unmercerized cotton does not show this phenomenon. Cotton mercerized with hydrochloric acid of sp. gr. 1.185 to 1.19 likewise took up more dye if washed and dyed previous to drying.[6]

The affinity of cellulose for dyestuffs is proportional to the colloidal activity produced by the moisture, *i.e.*, colloid water, normally present.[7] This affinity is reduced by dry heat and steam, but can be maintained or increased during such treatments by the presence of hygroscopic substances such as glycerine.

The increased affinity of mercerized cotton for dyes is due to the higher colloid state of the cellulose.[8] It requires from 40 to 50 per cent less of substantive dyestuffs than ordinary cotton to obtain the same depth of color.[9]

Cotton treated with sodium hydroxide of a sp. gr. of only 1.005 showed an increased affinity for the direct dye benzopurpurin

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[1] R. A. Gortner and W. F. Hoffman, *J. Am. Chem. Soc.*, **43** (1921), 2199.

[2] H. Rousset, *Rev. gén. sci. pur. appl.*, **20** (1909), 831.

[3] C. Beadle, *Chem. News*, **71** (1895), 213.

[4] S. H. Higgins, *J. Soc. Chem. Ind.*, **28** (1909), 188.

[5] E. Knecht, *J. Soc. Dyers Colourists*, **24** (1908), 107–109.

[6] E. Knecht, *Chem. Trade J.*, **56** (1915), 45.

[7] E. Justin-Mueller, *Färber-Ztg.*, **24** (1913), 98.

[8] W. P. Dreaper, *Chem. News*, **90** (1904), 179.

[9] W. Schaposchnikoff and W. Minajeff, *Z. Farben und Textilchem.*, **3** (1904), 163; **4** (1905), 81.

4B.[1] With solutions up to a sp. gr. of 1.09 the increase in affinity is roughly proportional to the concentration of the alkali; from sp. gr. 1.09 to 1.11 the increase in affinity is greater than the corresponding increase in the concentration of the alkali, this effect reaching a maximum at sp. gr. 1.13 to 1.15.

Gelatinized cellulose is dyed slightly or not at all by basic dyes.[2]

Gelatinization with Salts.—The use of zinc chloride for producing parchment paper was patented[3] in England in 1859. Paper was treated with a 76 per cent solution of the salt at a temperature of 27 to 100°. Its action is weaker than that of 76 per cent sulphuric acid.[4]

The use of zinc chloride for mercerizing was mentioned by Mercer in his original patent. Grandmougin[5] states that a solution of 72° Bé. produces, at 40 to 50°, effects similar to mercerization with sodium hydroxide; it is claimed by Minajeff,[6] however, that cotton treated with a zinc chloride solution of 64° Bé. (60.5 per cent) does not show a noticeably increased affinity for dyes. Cotton immersed in a 50 per cent solution of zinc chloride showed a shrinkage of 2.5 per cent.[7] Stretching produced a slight luster.

In the manufacture of vulcanized fiber, advantage is taken of the gelatinizing action of zinc chloride. Paper made from cotton is passed through a bath of zinc chloride of 70° Bé. at a temperature of 40°. It is then rolled up on heated drums to obtain the desired thickness, the heat causing gelatinization. The material is then leached to a chlorine content of less than 0.15 per cent. This process requires 3 to 4 weeks for material 0.25 inch thick, and 6 to 8 months for that 2 inches thick. The wet fiber is dried at 40 to 60°, pressed, and calendered. The shrinkage during drying and finishing is 50 per cent. The finished product has a sp. gr. of 1.1 to 1.48. Vulcanized fiber has a low resistance to water. In 24 hours it will take up from 25 to 70 per cent.[1] Red vulcanized fiber on prolonged contact with water absorbed 0.76 cubic centimeter in 34 days, and 0.62 cubic centimeter in 19 days, per cubic centimeter of fiber.[2] The increase in volume was 161 and 151 per cent respectively. Water at a temperature of 60° was absorbed more rapidly than cold, but the amount absorbed and the increase in volume was less than at ordinary temperature.

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[1] J. Hübner and W. J. Pope, *J. Soc. Chem. Ind.*, **23** (1904), 404–411.

[2] C. G. Schwalbe, *Z. angew. Chem.*, **20** (1907), 2172.

[3] Thomas Taylor, *Dinglers polytech. J.*, **155** (1860), 397.

[4] J. Ferwer, *Dinglers polytech. J.*, **159** (1861), 221.

[5] E. Grandmougin, *Bull. Mulhouse*, **68** (1898), 348; *Chem. Ztg.*, **32** (1908), 241.

[6] W. Minajeff, *Z. Farben-Ind.*, **9** (1910), 65.

[7] J. Hübner and W. J. Pope, *J. Soc. Chem. Ind.*, **23** (1904), 409.

Cellulose swells and becomes transparent in a saturated solution of sodium mercuric iodide. It forms a horny mass after being washed and dried.[3]

The mercerizing action of iodine salts was discovered by Hübner.[4] A concentrated solution of potassium iodide has about the same mercerizing action as a concentrated solution of sodium hydroxide. Washing with alcohol removed the potassium iodide completely. Saturated solutions of barium iodide and potassium mercuric iodide also produce mercerization.

According to von Weimarn,[5] any salt having a moderately high solubility in water can peptize[6] cellulose, provided certain conditions, such as concentration, pressure, temperature, and duration of action, are observed. In carrying out the peptization, 3 grams of cellulose, such as filter paper, and 100 cubic centimeters of water are placed in a vessel and heated, the salt being gradually added. Agitation hastens the conversion of the cellulose to a gelatinous plastic condition. With certain salts, such as calcium, barium, and strontium sulphocyanates, sodium, strontium, and calcium iodides, and calcium bromide, the process can be carried out by heating at atmospheric pressure. Sodium, potassium, and barium chlorides require heating at higher pressures. Peptization with a saturated solution of sodium chloride begins at a pressure of about 8 atmospheres, corresponding with a temperature of 170°.

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[1] C. Almy, *Met. Chem. Eng.*, **13** (1915), 746.

[2] F. H. Parker, *Phil. Mag.*, **25** (1913), 210.

[3] A. G. Duboin, *Compt. rend.*, **141** (1905), 385–388.

[4] J. Hübner and W. J. Pope, *J. Soc. Chem. Ind.*, **22** (1903), 70–77; **23** (1904), 409.

[5] P. P. von Weimarn, *Z. Chem. Ind. Kolloide*, **11** (1912),41–43; *Kolloid-Z.*, **29** (1921), 197–198, 198–199; G. P. 275882 (1912).

[6] Graham defined peptization as the conversion of a gel into a sol by means of a small quantity of a dispersing agent. In this chapter peptization is used in the broader sense of increasing the distance between particles.

Schwalbe[1] found that pure cellulose heated with a solution of sodium chloride at 180° for 3 hours did not swell or show indication of solution. He concludes that von Weimarn must have used an impure cellulose, such as absorbent cotton or filter paper.

Peptization of cellulose proceeds rapidly with boiling saturated solutions of LiCl, LiBr, LiI, $LiNO_3$, NaI, SrI_2, $Sr(CNS)_2$, $CaBr_2$, CaI_2, $Ca(CNS)_2$, $Ba(CNS)_2$, and $Mn(CNS)_2$. With salts that produce a very rapid peptization, such as the thiocyanates, a 1 per cent solution of cellulose forms a transparent jelly on cooling. Prolonged heating leads to degradation of the cellulose. Swelling and dispersion, at ordinary temperatures and pressures, proceed in the following order: NaCl, $BaCl_2$, KI, $SrCl_2$, $CaBr_2$, and LiCl. There is no noticeable swelling with sodium chloride after 5 years.

According to Herzog and Beck,[2] the dispersion of cellulose in strong solutions of the salts of the caustic alkalis and alkaline earths is a function of the hydration of the ions of the particular salt. Their effectiveness increases in the following order: NH_4, K, Na, Li, Ba, Sr, Ca, $\frac{1}{2}SO_4$, Cl, Br, I, CNS. Neither swelling nor solution takes place in the chlorides, bromides, nitrates, sulphates, thiocyanates, acetates, and lactates of Na, K, NH_4, and Mg; the bromides of Ba and Sr; or barium thiocyanate. Calcium thiocyanate is a very efficient solvent, though this property is not possessed by all thiocyanates.

A 30 per cent solution of sodium sulphide produced a shrinkage of 1.3 per cent in cotton. Stretching gave a slight luster.[3]

Adsorption of Salts.—Schönbein[4] observed that when strips of filter paper were dipped into solutions of acids, bases, and salts, the water always reached a greater height than the chemicals. When filter paper is spotted with aqueous solutions of the metallic salts, the area of concentration is greatly influenced by the kind of salt and paper, the temperature, and the concentration of the solution.[1] With strong solutions of copper sulphate the salt spreads all over the spot, while with dilute it concentrates in the middle. Cadmium salts have a marked tendency to spread over the entire wetted area.

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[1] C. G. Schwalbe, *Färber-Ztg.*, **24** (1913), 433.

[2] R. O. Herzog and F. Beck, *Z. physiol. Chem.*, **111** (1920), 287–292; *cf.* F. Beck, *Z. angew. Chem.*, **34** (1921), 113–114.

[3] J. Hübner and W. J. Pope, *J. Soc. Chem. Ind.*, **23** (1904), 409.

[4] C. F. Schönbein, *Chem. Zentr.*, **32** (1861), 881–884.

In slightly acid solution the metal ion of the salts of the heavy metals rises as high as the water, though this is not the case with neutral solutions.[2] The adsorptive power of filter paper is due mainly to the fact that is has the property of a coarse, disperse medium as the result of its distensible capillaries.[3] Cellulose behaves as a negative colloid, flocculating and adsorbing the positive colloids such as the sols of metallic hydroxides. The adsorption of neutral salts is very slight.

When vegetable fibers are treated with alkaline plumbate or plumbite solutions, lead oxide is fixed by them. The hydroxides of Cu, Zn, Co, and Fe''' can also be fixed directly. Cotton treated with Schweizer's reagent retains only traces of cupric oxide after washing; if the reagent contains sodium or potassium hydroxide, however, cupric oxide is fixed by the fiber.[4] In dilute cuprammonium solution, cotton shows a high preferential sorption of copper.[5] This may be due to chemical action.

When 1 gram of cellulose was immersed in 50 cubic centimeters of 1 per cent ferric chloride solution, filter paper fixed 0.229 per cent of iron, and cotton 0.112 per cent. Lower results were obtained with 0.1 per cent solution. With 1 per cent solutions of mercuric chloride and mercuric acetate, cotton fixed 0.2 and 1.5 per cent of mercury, respectively.[6] Cotton is capable of adsorbing and fixing small amounts of metal from dilute solutions of copper, nickel, aluminum, and potassium salts. Unbleached cotton shows this property to a greater extent than bleached.[7] The fixation is reduced to a minimum by treating the cotton with dilute sodium hydroxide and washing thoroughly. The phenomenon is shown to a greater extent by the artificial silks, and not at all by hydrocellulose. The adsorption of the salt solutions is independent of time, temperature, and concentration.

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[1] T. Bayley, *J. Chem. Soc.*, **33** (1878), 304–306; *cf.* Mansier, *J. pharm. chim.*, [6] **16** (1902), 60–64, 116–120.

[2] I. M. Kolthoff, *Pharm. Weekblad*, **57** (1920), 1515.

[3] K. Scherinja, *Pharm. Weekblad*, **57** (1920), 1289.

[4] A. Bonnet, *Compt. rend.*, **117** (1893), 518–519; **121** (1895), 700–701.

[5] H. F. Coward, L. Spencer, and F. C. Wood, *J. Textile Inst.*, **14** (1923), 529.

[6] W. Schellens, *Arch. Pharm.*, **243** (1905), 617–631.

[7] B. Rassow, *Z. angew. Chem.*, **24** (1911), 1127.

The source and purity of the cotton or other form of cellulose is of great influence. Haller[1] found negative adsorption with aluminum acetate, and in some cases with aluminum sulphate. With aluminum acetate, negative adsorption was least with raw cotton and increased with the purification of the fiber. With aluminum sulphate, the adsorption was positive with cotton in the raw state and after boiling with lime; however, boiling with caustic soda and bleaching caused negative adsorption. The adsorption of lead acetate was positive in all cases and increased with the purity of the fiber. Adsorption and fixation of the insoluble base do not necessarily run parallel. In every case there was a fixation of aluminum oxide with aluminum salts, even though negative adsorption values were sometimes obtained. According to Heermann,[2] the adsorption values recorded by Haller should be considered as "apparent adsorptions" consisting of the summation of adsorption and secondary reactions. The latter are sufficiently important in some cases as to show an apparent negative adsorption.

Durst[3] found that the fixation of alumina was influenced by such factors as the previous treatment of the cotton, time of immersion, concentration of the solution, temperature, and ratio of solution to cotton. Using bleached cotton and aluminum acetate, the adsorption of alumina was 0.064 per cent, as determined from the ash content of the cotton, and only 0.047 per cent calculated on the change in concentration of the solution.

When sulphite pulp was treated in a metal beater with 3 per cent of its weight of aluminum sulphate, the salt was quantitatively decomposed, all the alumina being fixed by the fiber.[4] Sutermeister[5] worked with poplar soda pulp, spruce sulphite pulp, and rag stock in glass. He found that the adsorption of alumina was independent of the concentration of the aluminum sulphate solution and that the amount adsorbed was in no case greater than 0.3 per cent of the weight of the fiber.

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[1] R. Haller, *Chem. Ztg.*, **42** (1918), 597; **43** (1919), 195.

[2] P. Heermann, *Chem. Ztg.*, **43** (1919), 195.

[3] G. Durst, *Chem. Ztg.*, **43** (1919), 374.

[4] C. G. Schwalbe and H. Robsahm, *Wochbl. Papierfabr.*, **43** (1912), 1454.

[5] E. Sutermeister, *Pulp Paper Mag. Can.*, **11** (1914), 803.

Tingle[1] has studied the same problem, using as cellulose acid-washed filter paper and bleached spruce sulphite pulp. With both neutral and basic solutions of aluminum sulphate, no change in the aluminum content of the solutions could be detected, except when a pulp contained calcium compounds and the wash water gave a distinctly alkaline reaction.

These findings have been recently confirmed by Schwalbe[2] in a reinvestigation in which non-metallic vessels were used. Neither cotton nor wood pulp adsorbed appreciable amounts of alumina from solutions of aluminum sulphate.

Cellulose in the colloidal condition produced by prolonged beating is capable of fixing metallic bases from aluminum sulphate and other salts.[3] Beaten hydrocellulose and oxycellulose possess this property to a high degree. The fixation of dyestuffs and metallic bases of neutral salts during the steaming or aging of mordanted materials is probably due to the formation of hydrocellulose and oxycellulose. The difficulty in wetting materials mordanted with metallic salts is caused by an irreversible state of the colloidal cellulose in combination with the metallic hydroxide.

Bancroft[4] states that all aluminum salts hydrolyze more or less readily in aqueous solution. The hydrolysis is greater with the weaker acids and increases with rising temperature. Cotton adsorbs alumina effectively only in basic solutions. Only colloidal alumina is taken up and firmly held by the fiber, coagulated alumina being held mechanically. It is probable that in all cases alumina and not a basic salt is adsorbed, though the phenomenon is complicated by the fact that alumina itself will adsorb some sulphuric acid. The increased adsorbing power of mercerized cotton is probably due to a structural difference in the fiber.

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[1] A. Tingle, *J. Ind. Eng. Chem.*, **14** (1922), 198.

[2] C. G. Schwalbe, *Z. angew. Chem.*, **37** (1924), 125.

[3] C. G. Schwalbe, *Z. angew. Chem.*, **32** (1919), 355.

[4] W. D. Bancroft, *J. Phys. Chem.*, **26** (1922), 501–536.

Kolthoff[1] found that practically no adsorption of metals took place from solutions of the alkali and alkaline earth salts. True adsorption of electrolytes by filter paper does not take place.[2] The phenomenon is a purely chemical one and depends on the ash content of the filter paper. The ash functions as a permutite: Ca-permutite $+ M^{++} \rightleftarrows$ M-permutite $+ Ca^{++}$. The metal may be Pb, Cu, Hg, Cd, Mn, or Fe. Silver, cobalt, and nickel are adsorbed to a less extent, and the alkali and alkaline earth ions not at all. This explains the prevalent belief that cellulose behaves as an acid and combines with metallic oxides.

Filter paper, according to Kolthoff,[3] showed negative adsorption of chlorine ions from sodium chloride. Masters[4] found that when pure neutral cellulose is extracted with sodium chloride and other neutral salts, an acid extract is obtained, while extraction of the cotton with water gives an alkaline solution. Extraction of 10 grams of cotton with a 20 per cent solution of sodium chloride gave 3.9 milligrams of hydrogen chloride. After washing the cotton free from alkali and chlorine ions, it again gave an acid extract with salt solutions. Temperature had no effect on the alkalinity and acidity obtainable. The occurrence of hydrochloric acid in the filtrate obtained by passing a sodium chloride solution through purified cotton had been previously observed by Harrison.[5]

Schwalbe[6] records a case where a gelatinized cotton pulp contained colloidal copper derived from the bronze knives in the beater. The pulp dyed bluish black, in place of the normal red color, with benzopurpurin 10B.

Gelatinization with Alkalis. Mercerization.—In a broad way, mercerization applies to the treatment of cellulose fibers with chemical reagents that produce swelling followed by shrinkage to dimensions below the original, on removal of the reagents. Technically, mercerization refers to the treatment of the fibers with strong caustic soda, the fibers being held under tension during the alkaline treatment or while the alkali is being removed by washing. Fibers so treated show a greatly increased luster when dry.

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[1] I. M. Kolthoff, *Pharm. Weekblad,* **58** (1920), 94.

[2] I. M. Kolthoff, *Pharm. Weekblad,* **57** (1920), 1515; **58** (1921), 152, 233.

[3] I. M. Kolthoff, *Pharm. Weekblad,* **58** (1921), 94.

[4] H. Masters, *J. Chem. Soc.,* **121** (1922), 2026.

[5] W. Harrison, *J. Soc. Dyers Colourists,* **27** (1911), 286.

[6] C. G. Schwalbe, *Z. Chem. Ind. Kolloide,* **2** (1908), 229.

The process is named from John Mercer, who was the first at least to appreciate its industrial possibilities. Mercer showed great aptitude for experimentation and was to the English dyeing trade of his day what Caro later became for the German dyestuff industry. In 1850 he took out a patent,[1] in which is stated:

> My invention consists in subjecting vegetable fabrics to the action of caustic soda or caustic potash, dilute sulphuric acid, or chloride of zinc, of a strength and temperature sufficient to produce new effects. I pass the cloth through a padding machine charged with caustic soda or caustic potash at 60 or 70° Twaddel's hydrometer, at the common temperature.

Mercer observed that the fabrics after removal of the alkali showed decided shrinkage, increased strength, firmness, and affinity for dyes. The ability of strong sodium hydroxide to produce shrinkage merely had been previously known in France.[2] Mercer, being apparently satisfied with the increased solidity and strength of his fabrics, did not employ tension; hence, luster was not apparent. In all justice it must be said that Thomas and Prevost,[3] in 1896, were the first to appreciate the silky luster attainable by mercerizing under tension, though the essentials of the process had been specified by Lowe.[4] He, however, was most concerned with preventing loss by shrinkage. Luster is not obtained unless the fibers are under tension during the alkaline treatment or while the alkali is being washed out.

When immersed in strong sodium hydroxide, the normally flat, twisted cotton fiber undergoes a great change. It swells to a cylindrical form, untwists, and contracts considerably in length. At the expense of the length, the walls become thicker and the lumen nearly disappears. The swelling in sodium hydroxide of a concentration of 15 to 20 per cent is sufficient to rupture the cuticle. The resulting bulges give a dumb-bell appearance. Technically, solutions containing 27 to 32 per cent of sodium hydroxide have been found most satisfactory for mercerization. In water, cotton swells in cross-section 40 to 42 per cent, and this is increased to 280 per cent in 20 per cent sodium hydroxide.[1]

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[1] John Mercer, E. P. 13296 (1850).

[2] J. Persoz, "Traité Théorique et Pratique de l' Impression des Tissus," III (1846), pp. 139–141.

[3] R. Thomas and E. Prevost, E. P. 20714 (1896).

[4] H. A. Lowe, E. P. 4452 (1890); *cf.* P. and C. Depoully, E. P. 28696 (1883); H. A. Lowe, E. P. 20314 (1889).

Paper made from cotton mercerized with 23 per cent sodium hydroxide, in comparison with untreated cotton, showed a decrease in stretch and tensile strength.[2] While the strength of the individual fibers is increased by mercerization, this treatment converts them into smooth cylinders that slip past one another, under tension, more easily than the normal twisted cotton fiber. Mercerization greatly increases the absorbency of the paper due to removal of the water-repellent incrustants.

Cotton increases in tensile strength from 30 to 50 per cent through mercerization. The increase is less when mercerization takes place under tension.[3] Krais[4] studied the shrinkage of cotton when treated with sodium hydroxide solutions of various strengths at 0, 10, and 20°. The maximum shrinkage of 31.3 per cent occurred with a solution of sp. gr. 1.320, and at a temperature of 10°.

Up to a concentration of $3N$, about the limit of solubility, lithium hydroxide produces greater shrinkage than equivalent concentrations of sodium and potassium hydroxides. The latter solutions produce about the same shrinkage up to $5N$; between $5N$ and $8N$, sodium hydroxide is more active than potassium hydroxide, but at greater concentrations potassium hydroxide is the more active. Tetramethyl-ammonium hydroxide produces considerable shrinkage at high concentrations, but none is obtained with ammonium hydroxide, hydrazine hydrate, calcium hydroxide, and barium hydroxide.[5]

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[1] R. S. Willows and A. C. Alexander, *J. Textile Inst.*, **13** (1922), 237.

[2] C. G. Schwalbe, K. Fenchel, and R. Cornely, *Wochbl. Papierfabr.*, **44** (1913), 757–759.

[3] R. S. Willows, T. Barratt, and F. H. Parker, *J. Textile Inst.*, **13** (1922), 229.

[4] P. Krais, *Z. angew. Chem.*, **25** (1912), 2649.

[5] E. Knecht and W. Harrison, *J. Soc. Dyers Colourists*, **28** (1912), 224.

While sodium hydroxide, due to its greater viscosity, has less mercerizing action than potassium hydroxide at high concentrations, under ordinary conditions 1 gram-molecule of sodium hydroxide is equivalent in its action to 1.5 gram-molecules of potassium hydroxide.[1]

The heat liberated during mercerization increases with the concentration of the sodium hydroxide but is not proportional to it.[2] There are two breaks in the curve, the first between 10 and 15 per cent sodium hydroxide and the second at about 30 per cent sodium hydroxide.

Mercerization appears to be complete in about 3 minutes.[3] It is stated to be instantaneous and that immersion for a period longer than 1 minute is useless.[4] Between 40 and 180 seconds, there is not much difference in mercerization in so far as the dyeing capacity of the cotton is concerned.[5]

While various theories have been advanced to account for the luster of mercerized cellulose, it is generally accepted that this is due to the production of a smooth surface from which the light is reflected,[6] and to translucency of the cell wall. The more nearly round the fiber, the greater is the luster.[7] Hübner and Pope[8] found that the untwisting of the ribbon-like cotton fiber is of great importance. They attributed the luster to a series of spiral ridges that reflect the light. This is improbable, since fibers mercerized with just enough tension to keep them straight are without luster.

The alkali-cellulose fiber, on washing with water, becomes inelastic and cannot be stretched to its original length without breaking. If washed with ammonia, however, the fiber retains its elasticity. This also becomes inelastic on washing with water. If the fiber is under tension while the ammonia is being washed out, it acquires a luster.[1] This is probably explainable on the observation of Coward and Spencer[2] that there is marked hysteresis in the shrinkage of cotton fiber on replacing solutions of mercerizing strength with weaker ones.

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[1] E. Ristenpart, C. A., **15** (1921), 2728.

[2] T. Barratt and J. W. Lewis, *J. Textile Inst.*, **13** (1922), 113.

[3] R. S. Willows *et al*, *l.c.*

[4] F. J. G. Beltzer and J. Persoz, "Les Matiéres Cellulosiques" (1911), p. 62.

[5] E. Knecht, *J. Soc Dyers Colourists*, **24** (1908), 68.

[6] H. Lange, *Färber-Ztg.*, **9** (1898), 197; W. Harrison, *J. Soc. Dyers Colourists*, **31** (1915), 198; T. Barratt, *J. Soc. Chem. Ind.*, **43** (1924), 593B.

[7] A. Adderly, *J. Textile Inst.*, **15** (1924), 195T.

[8] J. Hübner and W. J. Pope, *J. Soc. Chem. Ind.*, **23** (1904), 410.

Vieweg[3] found that cellulose absorbs more alkali from a solution of sodium hydroxide saturated with sodium chloride than without it. Whether this is true or not appears to depend upon the temperature and the particular concentration of the solution in sodium hydroxide and salt.[4] According to Miller,[5] sodium chloride and sodium carbonate in small amounts are without effect. It is well established, however, that the presence of sodium chloride reduces the shrinkage and luster,[6] and the affinity for dyestuffs; [7] hence the degree of gelatinization. Hübner[6] observed the following differences:

	Shrinkage, Per Cent
Sodium hydroxide, 12 per cent	11.5
Sodium hydroxide, 12 per cent, saturated with NaCl	6.8
Sodium hydroxide, 20 per cent	18.6
Sodium hydroxide, 20 per cent, saturated with NaCl	15.7

Sodium silicate[8] also reduces the mercerizing action of sodium hydroxide.

Alkali-cellulose. Adsorption of Alkalis.—There has been much dispute as to whether sodium hydroxide forms a definite compound with cellulose. Many investigators have failed to find evidence of a chemical compound.[9] Through its reaction with chromic acid mixture, Thies[1] deduces that no alkali-cellulose compound is formed. Compounds such as sodium ethylate give decidedly more carbon dioxide on oxidation in a given time than a simple mixture of alkali and alcohol. Gladstone's soda-cellulose by this test does not behave differently from pure cellulose.

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[1] E. Thiele, *Chem. Ztg.*, **25** (1901), 610.

[2] H. F. Coward and L. Spencer, *J. Textile Inst.*, **14** (1923), 32.

[3] W. Vieweg, *Ber.*, **41** (1908), 3269.

[4] C. Beadle and H. P. Stevens, *Eighth Int. Cong. Appl. Chem.*, **13** (1912), 37; *J. Soc. Dyers Colourists*, **30** (1914), 244.

[5] O. Miller, *J. Russ. Phys.-Chem. Soc.*, **37** (1905), 361; *Ber.*, **41** (1908), 4302.

[6] J. Hübner, *J. Soc. Chem. Ind.*, **28** (1909), 228; W. Herbig, *Färber-Ztg.*, **23** (1912), 136.

[7] E. Knecht, *J. Soc. Chem. Ind.*, **28** (1909), 228.

[8] J. Hübner and W. J. Pope, *J. Soc. Chem. Ind.*, **23** (1904), 409; W. Herbig, *Färber-Ztg.*, **23** (1912), 136; P. Gardner, "Mercerisation der Baumwolle" (1898), p. 44.

[9] C. Beadle and H. P. Stevens, *J. Soc. Dyers Colourists*, **30** (1914), 244; A. Leighton, *J. Phys. Chem.*, **20** (1916), 32; H. F. Coward and L. Spencer, *J. Textile Inst.*, **14** (1923), 32.

Karrer[2] maintains that a definite addition compound, $C_{12}H_{20}O_{10}$.-NaOH, remains after treating cellulose with concentrated sodium hydroxide and washing with alcohol. The more recent papers are in entire agreement with this view.[3] According to Vieweg,[4] alkali-cellulose behaves precisely as an alcoholate in its reactions with carbon bisulphide and benzoylchloride. Gelatinization evidently produces some change in the cellulose molecule. Vignon[5] found the following heats of combustion for precipitated and mercerized cellulose:

	Calories
Purified cotton (dried at 110°)	4,223
Precipitated cellulose (from Schweizer's reagent)	3,982
Mercerized cellulose	3,980

Lowering of the heat of combustion was believed to be due to depolymerization.

Mercerization causes "depolymerization" of the cellulose molecule with decomposition into water and carbon dioxide on long standing.[6] Mercerized sulphite cellulose prepared for viscose showed the following changes:

	Cellulose, per cent	NaOH, per cent	Na_2CO_3, per cent	H_2O, per cent
Alkali-cellulose, fresh	24.48	15.36	1.72	58.44
Alkali-cellulose, after standing 3 years at 15° in the absence of air	19.40	6.40	7.95	66.25

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[1] F. H. Thies, *Färber-Ztg.*, **24** (1913), 393.

[2] P. Karrer, *Cellulosechemie*, **2** (1921), 125.

[3] W. Vieweg, *Z. angew. Chem.*, **37** (1924), 1008–1010; E. Heuser, *Ibid.*, 1010–1013; F. Dehnert and W. König, *Cellulosechemie*, **5** (1924), 107–112; E. Knecht and J. H. Platt, *J. Soc. Dyers Colourists*, **41** (1925), 53–55.

[4] W. Vieweg, *Zellstoff u. Papier*, **2** (1922), 18.

[5] L. Vignon, *Compt. rend.*, **131** (1900), 708.

[6] H. Eggert, *Kunststoffe*, **3** (1913), 381.

The cellulose had decomposed to the extent of losing its fibrous structure.

Cellulose mercerized with 17 per cent sodium hydroxide under tension, when examined by the X-ray method, gives a point diagram like the original fiber. If the fiber is not under tension, Debye-Scherrer rings, not a point diagram, result, showing that the crystallites occur in every possible position in the fiber. Any slight difference between the original fiber and that mercerized under tension may be due to the migration of an oxygen bridge in the cellulose molecule.[1] Gebhard[2] has suggested that mercerization results in enolization.

Gladstone[3] treated cotton with strong sodium hydroxide and washed it with cold absolute alcohol or hot alcohol of sp. gr. 0.825. The alkali remaining in the fiber agreed with the formula $C_{12}H_{20}O_{10}.NaOH$ and was considered as combined. Thiele,[4] by the arbitrary method of a limited washing with strong ammonia of cotton treated with 30 per cent sodium hydroxide, concluded that the compound $C_{12}H_{20}O_{10}.2NaOH$ was formed. Cross and Bevan[5] state that a definite reaction takes place in the molecular ratio $C_{12}H_{20}O_{10}:2NaOH$. The latter becomes $C_{12}H_{20}O_{10}.NaOH$ on washing with alcohol.

Vieweg,[6] in 1907, shook cotton with solutions of sodium hydroxide of various strengths and determined the amount of alkali absorbed by the cotton, by titrating a portion of the liquid. The curve obtained on plotting the amount of sodium hydroxide absorbed against the concentration of the original solution showed two definite breaks. The first break was obtained at concentrations of 16 to 24 grams of sodium hydroxide per 100 cubic centimeters of solution, corresponding with an absorption of 13 per cent of alkali by the cellulose and a molecular ratio of $(C_6H_{10}O_5)_2: NaOH$. The second break was obtained at concentrations of 35 grams and greater per 100 cubic centimeters, corresponding with an absorption of 24 per cent of sodium hydroxide and a molecular ratio of $(C_6H_{10}O_5)_2 : 2NaOH$.

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[1] R. O. Herzog and G. Londberg, *Ber.*, **57** (1924), 329.

[2] K. Gebhard, *Chem. Ztg.*, **37** (1913), 663.

[3] J. Gladstone, *J. Chem. Soc.*, **5** (1853), 17.

[4] E. Thiele, *Chem. Ztg.*, **25** (1901), 610.

[5] C. F. Cross and E. J. Bevan, "Cellulose" (1895), p. 23.

[6] W. Vieweg, *Ber.*, **40** (1907), 3876–3883; *cf. Ibid.*, **41** (1908), 3269–3275.

Miller[1] worked in essentially the same way as Vieweg but instead obtained a smooth curve. He claimed that the Gladstone compound did not exist and that the action of strong sodium hydroxide on cotton was a solid-solution phenomenon.[2] Hübner and Teltscher[3] likewise came to the conclusion that "soda-cellulose" as a definite compound does not exist. Hot absolute alcohol was found to remove practically all of the sodium hydroxide. The results of Gladstone were due to his failure to wash the cotton with cold absolute alcohol until equilibrium had been reached. Their own results on adsorption, wherein the cotton was washed with alcohol, have been criticized on the ground that the amount of caustic soda removed by the alcohol is a function of the temperature; and further that the method gives no definite indication of the true adsorption in aqueous solution.

The question was carefully investigated by Leighton,[4] who obtained smooth adsorption curves and found no evidence whatever of a definite chemical compound. If cotton is shaken with alkali, a portion of the supernatant liquid analyzed, and the amount of adsorption calculated from the decrease in concentration, the adsorption figure is not accurate unless no liquid is taken up by the cotton. Obviously, this is not possible. A direct or gravimetric method of determining the adsorption will give too high results unless all the unadsorbed solution is removed. If the cotton takes up water and alkali in the same ratio as they exist in the solution, no adsorption occurs. Leighton shook cotton with alkali for 3 hours and to avoid obvious errors centrifuged it for 1 hour at 4000 r.p.m.

Below a concentration of 90 grams of sodium hydroxide per liter, no adsorption takes place. For a concentration of 300 grams per liter there is obtained an adsorption of 0.27 gram of sodium hydroxide per gram of cotton by analyzing the solution, and an

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[1] O. Miller, *Ber.*, **40** (1907), 4903; **41** (1908), 4297; *Chem. Ztg.*, **29** (1905), 491.

[2] O. Miller, *Ber.*, **43** (1910), 3430.

[3] J. Hübner and F. Teltscher, *J. Soc. Chem. Ind.*, **28** (1909), 641–644.

[4] A. Leighton, *J. Phys. Chem.*, **20** (1916), 32–50.

Adsorption of NaOH by Cotton

Volume of solution = 100 cubic centimeters; weight of cotton = 1.0 to 1.2 grams; time of run = 3 hours

Solution, grams NaOH per liter	Grams NaOH adsorbed per gram cotton		Solution, grams NaOH per liter	Grams NaOH adsorbed per gram cotton	
	Gravimetric	Titrametric		Gravimetric	Titrametric
474	0.916	....	230	0.664	
450	.....	0.28	212	0.642	
427	0.887	....	210	.....	0.19
415	0.875	....	190	0.594	
400	.....	0.27	189	0.579	
379	0.846	....	184	0.572	
350	.....	0.27	175	.....	0.12
323	0.782	....	140	.....	0.08
300	.....	0.27	138	0.461	
276	0.733	....	125	0.433	
275	.....	0.25	90	.....	0.01
231	0.665	....	40	.....	0.00

adsorption of 0.75 gram by analyzing the centrifuged cotton. There is thus a marked difference between the titration curve and the gravimetric curve. The latter is much more accurate than the former, though the true adsorption curve must lie between them.

According to Kolthoff,[1] cellulose takes up sodium hydroxide and potassium hydroxide from solutions up to 2*N*, in accordance with the partition law. Between 2*N* and 6*N* the amount taken up increases greatly but is independent of the concentration; while between 6*N* and 8*N* there is a further decided increase; it is likewise independent of the concentration. He concludes that adsorption in the true sense does not take place but that chemical combination occurs.

Harrison[2] attributes failure to follow the ordinary adsorption formula to the change in the physical state of the fiber produced by certain concentrations of caustic soda. In the case of regenerated cellulose, maximum absorption of water and caustic soda takes place in a 9 per cent solution of sodium hydroxide, while with cotton a 17.5 per cent solution is required. This is due to the resistance to swelling of the cotton cuticle, a condition obtaining until the concentration of the alkali is sufficient to cause it to burst.[1] Mercerization does not destroy the cuticle.[2]

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[1] I. M. Kolthoff, *Pharm. Weekblad*, **58** (1921), 46–56.

[2] W. Harrison, *J. Soc. Dyers Colourists*, **31** (1915), 198.

The effect of mechanical hindrance in studying adsorption is of great importance. While there are certain objections to its use, regenerated cellulose should be the most suitable material. Cotton loose and in the form of fabric, absorbs the same amount of water; however, loose cotton absorbs about twice as much sodium hydroxide as the fabric.[3] The swelling of cotton fibers in solutions of sodium hydroxide is about equal to the volume of liquor absorbed, the limit of swelling being set by the cuticle. In sodium hydroxide solutions up to 14 per cent, both sodium hydroxide and water are absorbed rapidly and according to the strength of the solutions. Above 14 per cent, the cotton continues to take up sodium hydroxide, but less rapidly, while there is a distinct decrease in the absorption of water.

The "hydration" and sodium hydroxide absorption were determined by Beadle and Stevens[4] with regenerated cellulose (cuprammonium). Skeins were immersed in sodium hydroxide and weighed after removal of the surface liquid. The weight of alkali, determined by titration, subtracted from the total increase in weight of the skeins gave the "hydration" or water absorbed. The data given in the table below represent combined adsorption and absorption phenomena. They are interesting in that they show how much water and sodium hydroxide are taken up by cellulose under certain conditions. The maximum amounts of both substances taken up are attained by a 9.0 per cent solution of sodium hydroxide at a temperature of 5°.

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[1] C. Beadle and H. P. Stevens, *J. Soc. Dyers Colourists*, **30** (1914), 244.

[2] W. Minajeff, *Z. Farben-Ind.*, **7** (1908), 1, 21.

[3] H. F. Coward and L. Spencer, *J. Textile Inst.*, **14** (1923), 32.

[4] C. Beadle and H. P. Stevens, *Eighth Int. Cong. Appl. Chem.*, **13** (1912), 25.

Per cent NaOH in bath	Hydration, cellulose = 100			NaOH absorption, cellulose = 100		
	At 5°	At 20°	At 40°	At 5°	At 20°	At 40°
1	217	182	167	3	3	3
2	279	217	192	8	8	8
3	324	241	216	16	14	14
4	426	280	224	24	16	16
5	615	300	230	42	22	17
6	1,380	310	238	83	25	20
7	1,960	380	240	150	36	25
8	2,576	562	261	224	56	30
9	2,699	758	338	256	74	38
10	1,800	920	440	210	98	56
11	1,483	861	458	182	110	66
12	1,310	719	480	170	112	72
13	1,200	620	412	161	102	76
14	1,003	558	360	142	96	78
15	798	500	334	132	88	74
16	762	458	310	128	84	72
17	715	420	300	124	82	71
18	658	400	280	122	82	70
20	590	360	240	110	84	72
22	540	325	220	114	86	73
25	461	280	220	120	86	76

It is an old observation[1] that when solutions of the hydroxides of barium, strontium, and calcium are passed through filter paper adsorption of the base takes place. Cellulose in a $\frac{N}{5}$ solution of barium hydroxide at 0° took up 3.82 per cent of the base; in a $\frac{N}{10}$ solution of strontium hydroxide at 0°, 2.18 per cent.[2] Vignon[3] found that 100 grams of cotton fixed 2.67 grams of barium hydroxide from a 1.0 per cent solution, and 0.39 gram from a 0.1 per cent solution.

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[1] A. Müller, *J. prakt. Chem.*, **83** (1861), 384; H. Weiske, *Landw. Vers.-Sta.*, **19** (1876), 155.

[2] H. Wichelhaus and W. Vieweg, *Ber.*, **40** (1907), 441.

[3] L. Vignon, *Compt. Rend.*, **143** (1906), 550.

Kolthoff[1] obtained no adsorption with sodium and potassium carbonate solutions up to $0.5N$. Ammonium hydroxide was taken up in small quantity from solutions up to $6N$, but independently of the concentration. Barium hydroxide was taken up in amounts proportional to the square roots of the final concentrations.

Grimm,[2] in studying the action of caustic alkalis and alkaline earths, found that the greatest adsorption takes place in 4 to 6 hours, after which there is a decrease. The greater the concentration of the solution the greater is the adsorption. With some bases motion increases adsorption while with others it decreases it. The alkaline earths were strongly adsorbed, the caustic alkalis only weakly so.

Bleached cotton	Per cent adsorbed based on weight of fiber				
	CaO	SrO	BaO	K_2O	Na_2O
Standing	1.00	2.04	4.08	0.72	0.63
Shaking	1.72	2.83	2.52	0.48	0.32

Ammonia is retained by cellulose fibers.[3] Filter paper[4] in an atmosphere containing ammonia will take up detectable amounts. Cotton will take up 115 times its volume of ammonia at atmospheric pressure.[5] Dry ammonia is adsorbed by dry cellulose[6] in approximately the ratio $NH_3:4C_6H_{10}O_5$.

Vignon[7] heated ammonium hydroxide of 22° Bé. and cellulose in sealed tubes. Between 100 and 200° combination took place with the fixation of 1.05 to 2.86 per cent of nitrogen. The presence of an amino group in the cellulose was indicated by an affinity of the compound for acid dyes, and by the heat of reaction with sulphuric acid. Ammonia at elevated temperatures readily attacks the artificial silks, especially Chardonnet, reducing it to a powder having the properties of aminocellulose.[1] The formation of an amino group requires confirmation.

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[1] I. M. Kolthoff, *Pharm. Weekblad,* **58** (1921), 46.

[2] H. Grimm, *Zellstoff u. Papier,* **1** (1921), 33–56.

[3] Mansier, *J. pharm. chim.,* **16** (1902), 61.

[4] H. R. Procter, *J. Soc. Chem. Ind.,* **23** (1904), 9; L. L. de Koninck, *Bull. soc. chim. Belg.,* **23** (1909), 221.

[5] F. H. Bowman, "The Structure of the Cotton Fibre," London (1908), p. 201.

[6] B. Oddo, *Gazz. chim. ital.,* **49**, II (1909), 127.

[7] L. Vignon, *Compt. rend.,* **112** (1891), 487.

The action of dilute sodium hydroxide at various temperatures has been studied by Schwalbe and Robinoff.[2] This is very slight for pure cotton but becomes considerable with chemically modified material. The cotton was purified by heating with alkaline rosin soap, washing with hot water, and carefully bleaching. It had a corrected copper number of 0.04. With concentrations up to 7 per cent, a 4 per cent solution of the alkali had the most drastic action at room temperature. The copper number of the cotton so treated was 0.257. The solubility decreased with increase in concentration, becoming inappreciable with 9.0 per cent sodium hydroxide. The solubilities were:

	NaOH solution, per cent								
	1	2	3	4	5	6	7	8	9
Solubility, per cent	0.74	0.53	0.49	0.42	0.34	0.30	0.14	0.06	

The copper numbers of the cotton treated with sodium hydroxide at various temperatures were:

Temperature	Strength of NaOH solution, per cent				
	1	2	3	4	5
	Copper numbers				
Room..........................	0.150	0.166	0.195	0.257	0.135
100...........................	0.180	0.200	0.262	0.528	0.168
135...........................	0.142	0.170	0.395	0.890	0.285
150...........................	0.100	0.150	0.280	0.700	0.120
179...........................	.....	0.110	0.128	0.445	0.050
213...........................	.....	.....	.....	.....	0.000

Cold and hot alkali up to 100° has little effect, but above this point the action increases with rise in temperature. Judging from the copper number, 4 per cent sodium hydroxide has the greatest effect at elevated temperatures also. The gum values, *i.e.*, the amount of flocculent material precipitated by alcohol after neutralization of the alkaline extracts, increased greatly above 150°, so that this appears to be the critical temperature. The alkali presumably decomposes the cellulose with the formation of substances related to hydrocellulose.

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[1] F. J. G. Beltzer and J. Persoz, "Matiéres Cellulosiques," p. 104.

[2] C. G. Schwalbe and M. Robinoff, *Z. angew. Chem.*, **24** (1911), 256–258.

Tests for Mercerization.—The use of iodine solutions has been mentioned. The reaction with substantive dyes is useful. Ordinary cotton dyed with benzopurpurin 4B is turned blue immediately by hydrochloric acid while mercerized cotton becomes reddish violet.[1] On reduction by heating with titanous chloride, ordinary cotton appears indigo blue and mercerized cotton, red just prior to complete destruction of the color. To obtain this difference the cotton must be treated with caustic soda of a specific gravity greater than 1.15; if stretched during mercerization, the specific gravity must be over 1.175. Knaggs[2] found that reduction is not necessary. If strong hydrochloric acid is added to the dilute dye bath, in which the samples are immersed, until the shade of the unmercerized sample just becomes blue, the mercerized cotton remains a bright red.

The degree of mercerization[3] can be determined by dyeing the cotton with benzopurpurin 4B, the amount of dyestuff taken up being estimated by indirect titration.[4] Hanks, treated under tension in caustic soda solutions of various strengths, were dyed together in the same bath. The fibers then contained the following amounts of dye:

Specific gravity, NaOH solution	Dye, per cent	Specific gravity, NaOH solution	Dye, per cent
1.05	1.88	1.225	3.27
1.10	2.39	1.25	3.38
1.125	2.57	1.275	3.50
1.15	2.95	1.30	3.56
1.175	3.02	1.325	3.60
1.20	3.15	1.35	3.66

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[1] E. Knecht, *J. Soc. Dyers Colourists*, **24** (1908), 67.

[2] A. B. Knaggs, *J. Soc. Dyers Colourists*, **24** (1908), 112.

[3] E. Knecht, *J. Soc. Dyers Colourists*, **24** (1908), 68.

[4] E. Knecht, *J. Soc. Dyers Colourists*, **21** (1905), 3.

Ordinary cotton took up 1.77 per cent of the dye. Thus, the amount of dye taken up augments with the increase in the strength of the caustic soda.

Miller[1] found that increased adsorption of dyes began with cotton treated with 9 per cent caustic soda. The adsorption increased to a maximum lying beyond 25 per cent caustic soda.

Vieweg[2] has proposed a method for testing mercerization based on the adsorption of dilute alkali. One gram of the material is shaken in a wide-mouthed bottle with 100 cubic centimeters of $\frac{N}{2}$ sodium hydroxide for 30 minutes, and a portion of the liquid withdrawn and titrated with $\frac{N}{2}$ acid. Ordinary cotton adsorbs 1.0 per cent of sodium hydroxide. The adsorption reaches 2.8 with cotton that has been mercerized with 16 per cent sodium hydroxide, but does not exceed 2.9 with cotton mercerized with 50 per cent alkali. Some forms of cellulose show a higher adsorption. Obviously, the "adsorption" is not only influenced by the degree of gelatinization but by the extent to which the alkali may react chemically with the modified celluloses.

	NaOH, per cent		NaOH, per cent
Pure cellulose	1.0	Filter paper	1.6
Sulphite pulp	1.2	Regenerated cellulose, cuprammonium	4.0
Soda pulp	1.6		
Sulphate pulp	1.7	Viscose	4.5

Briggs[3] has shown that the adsorption is much greater in alcoholic solutions of sodium hydroxide and increases with the strength of the alcohol. Artificial silks show an adsorption as high as 14 to 15 per cent, based on the cellulose, in $\frac{N}{2}$ sodium hydroxide solution in 93 per cent alcohol. With the latter solution, it is possible to show differences in the degree of gelatinization attained by beating pulp in a Hollander.

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[1] O. Miller, *Ber.*, **43** (1910), 3430; *cf.* J. Hübner and W. J. Pope, *J. Soc. Chem. Ind.*, **23** (1904), 404.

[2] W. Vieweg, *Ber.*, **40** (1907), 3876; *Chem. Ztg.*, **32** (1908), 329; *Papier-Ztg.*, **34** (1909), 1352.

[3] J. F. Briggs, *Chem. Ztg.*, **34** (1910), 455.

Gelatinization with Acids.—The parchmentizing action of strong mineral acids has been discussed elsewhere (Chap. IX). While they have a mercerizing effect, the luster is not comparable to that obtained with the caustic alkalis. The mercerized product is harder, and without due care gelatinization is soon followed by hydrolysis.

Mercer[1] used sulphuric acid of 105° Tw. (sp. gr. 1.525 or 62 per cent) at a temperature not exceeding 50°F. Thomas and Prevost[2] specify acid of sp. gr. 1.518 to 1.62. Sulphuric acid of sp. gr. 1.526 to 1.611, and phosphoric acid of sp. gr. 1.70 give to cotton, with the exception of luster, properties very similar to those obtained by mercerization with sodium hydroxide.[3]

In addition to sulphuric acid, Hübner and Pope[4] worked with phosphoric, nitric, and hydrochloric acids. Concentrated hydrochloric acid and nitric acid of sp. gr. 1.415 produced a contraction of the cotton of 9.5 per cent. A slight luster was obtained by tension. Cold hydrochloric acid, sp. gr. 1.16 to 1.18, has practically no effect on cotton fiber.[5] It is strongly attacked by acid of sp. gr. 1.195 to 1.20. Acid of sp. gr. 1.185 to 1.19 shrinks the fiber and greatly increases its affinity for dyes. The specific gravity of an acid reading 1.185 is reduced to 1.18, indicating that a preferential adsorption of hydrogen chloride takes place.

Cotton treated with nitric acid of sp. gr. 1.41 shows many of the properties of mercerization.[6] Mercerizing action does not begin at the ordinary temperature with acid below a sp. gr. of 1.38. The most suitable strength is 1.415. Acids of sp. gr. 1.11 to 1.31 have a tendering action.[7]

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[1] J. Mercer, *l.c.*

[2] R. Thomas and E. Prevost, E. P. 18040 (1895).

[3] E. Grandmougin, *Z. Farben-Ind.*, **6** (1907), 2; *cf. Chem. Ztg.*, **32** (1908), 241.

[4] J. Hübner and W. J. Pope, *J. Soc. Chem. Ind.*, **23** (1904), 409.

[5] E. Knecht, *J. Soc. Dyers Colourists*, **31** (1915), 8; *Chem. Trade J.*, **56** (1915), 45.

[6] E. Knecht, *J. Soc. Dyers Colourists*, **12** (1896), 89.

[7] E. Knecht, *Ber.*, **37** (1904), 549.

Adsorption of Acids.—Girard[1] treated hemp fibers with a very dilute solution of hydrochloric acid and dried them at 45°. They were then heated at 140° in a glass tube through which passed a current of air. The latter did not render a solution of silver nitrate turbid. The fibers were, however, converted into brittle hydrocellulose, from which all the acid was subsequently recovered. Cellulose may be tendered by acids, and yet it is very difficult to detect them.[2]

Sulphuric acid can be readily removed from cellulose by washing, while the more volatile acids, such as hydrochloric, nitric, sulphurous, and acetic, are not only resistant to washing but to drying as well. Koechlin[3] likens this behavior to the adsorption of gases in a porous substance such as charcoal. Washing with water will not remove even small quantities of acetic acid from cotton, so that it is neutral to litmus.[4] To accomplish this end the moist cotton must be treated for an hour with superheated steam at a temperature of about 200°.

Acid is more rapidly removed from cotton by washing it with a solution of sodium chloride than with pure water.[5]

Vignon[6] found that when cotton was immersed in 1.0 and 0.1 per cent sulphuric acids, all the acid could be completely removed by washing with water.

It is well known that filter paper will take up acids existing in the atmosphere of the laboratory. Cellulose dried over fused calcium chloride and treated with dry hydrogen choride in anhydrous ether, after washing with anhydrous ether, showed an adsorption of 0.46 per cent of hydrogen chloride.[7]

Cotton exposed to a stream of nitric oxide for 24 hours took up 2.40 per cent of the gas.[8] It retained 1.67 per cent nitric oxide after exhaustion by exposure in a desiccator containing sulphuric acid and a dish with ferrous sulphate and lime.

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[1] A. Girard, *Ann. chim. phys.*, [5] **24** (1881), 356.

[2] J. Hübner, *J. Soc. Chem. Ind.*, **34** (1915), 935.

[3] C. Koechlin, *Bull. Mulhouse*, **58** (1888), 547.

[4] W. Zänker and O. Mann, *Färber-Ztg.*, **27** (1916), 355.

[5] H. F. Coward and G. M. Wigley, *J. Textile Inst.*, **13** (1922), 121.

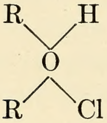
[6] L. Vignon, *Compt. rend.*, **143** (1906), 550.

[7] H. Jentgen, *Z. angew. Chem.*, **29** (1910), 1544.

[8] T. Panzer, *Z. physiol. Chem.*, **93** (1915), 388.

Oddo[1] found that dry hydrogen chloride combined with cellulose in the definite ratio of one molecule of the gas to every $(C_6H_{10}O_5)_4$. The other gases tested did not show this relationship. They were taken up in the order of their solubility in water, namly, HCl, H_2S, N_2O, CO_2, C_2H_2, CO, O, N, CH_4, and H. The order of absorption is comparable to that with charcoal. Nitrated cellulose (13.32 per cent nitrogen) absorbed about five times the volume of sulphur dioxide taken up by cellulose. Since the hydrogen chloride could not be displaced by an indifferent gas, it is assumed that a compound is formed of the nature of an oxonium derivative (I), or one similar to that obtainable with aldehydes (II).

I



II

$$R.CH{:}O + HCl = R.CHCl.OH$$

Kolthoff,[2] working with aqueous solutions of hydrochloric, sulphuric, acetic, and oxalic acids in concentrations of 0.1*N* or less (0.5*N* or less for oxalic acid), found that the amount of the acid taken up by filter paper was almost exactly equivalent to the alkalinity of the ash of the paper.

Hydrochloric, phosphoric, and sulphuric acids in moderate concentrations do not form compounds with cellulose at the

Solution, grams HCl per liter	Adsorption of HCl, grams per 100 grams of cellulose	
	Gravimetic	Titrametric
45.8	2.0	0
114.5	3.1	0
209.2	6.2	2.34
288.9	6.9	7.00
331.3	7.3	9.28
373.6	9.1	11.63
414.0	. . .	13.97

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[1] B. Oddo, *Gazz. chim. ital.*, **49**, II (1919), 127.

[2] I. M. Kolthoff, *Pharm. Weekblad,* **57** (1920), 1571.

ordinary temperature. Leighton[1] found that selective adsorption was most marked with hydrochloric acid and less with sulphuric acid. There was none with phosphoric acid. The procedure followed in this work was similar to that used with sodium hydroxide. A solution of sulphuric acid up to a concentration of 400 grams per liter is absorbed as such. According to Coward,[2] cotton shows a preferential sorbtion of acid from a dilute solution of sulphuric acid.

Gelatinization by Beating.—Soon after sulphite pulp became an article of commerce, it was found that prolonged beating produced a slimy mass suitable for making "pergamyn," *i.e.*, imitation parchment and greaseproof papers.[3] If grinding or beating is continued until the fibrous structure is destroyed, a 4 per cent suspension has the consistency of thick honey. Evaporation of the water at a temperature below 40° leaves a hard, horny mass known as "cellulith."[4] Its density varies from 1.4 to 1.5.

Gelatinization in a beater is due to both a brushing and a cutting action. Mere comminution produces a more apparent than real gelatinization; hence it is advisable to use dull knives that have a pounding rather than a cutting action. The pounding and brushing effects are increased by having the stock in the beater of the highest practical concentration. This is about 4 per cent for the ordinary Hollander. The rate of gelatinization is slow at first and then increases rapidly.

Fibers that have been completely dried gelatinize or "hydrate" less readily than those that have been preserved in the wet state. This is particularly true of ground wood, as is shown by the difficulty frequently encountered in separating the fibers in the beater. Some "hydration" takes place on the prolonged standing of pulp in water, but the extent can be but very slight. It is stated, however, that in the manufacture of newsprint where the machine operates at speeds of 600 to 1000 feet per minute, the extra hydration resulting from allowing the pulp to stand in the stock tanks for 24 hours, is sufficient to cause sticking to the presses of the machine.[1] This change may be due to bacterial action.

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[1] A. Leighton, *J. Phys. Chem.*, **20** (1916), 188–194.

[2] H. F. Coward, L. Spencer, and F. C. Wood, *J. Textile Inst.*, **14** (1923), 529T.

[3] S. Ferenczi, *Z. angew. Chem.*, **12** (1899), 51.

[4] H. Brunswig, U. S. P. 622325 (1899); C. D. Abel, E. P. 18930 (1897); M. M. Rotten, G. P. 98201 (1897).

In Germany the gelatinized Mitscherlich sulphite pulp used in the manufacture of pergamyn is known as cellulose mucilage (Zellstoffschleim). Hofmann[2] attempted to find a chemical difference between pergamyn pulp and the wood pulp from which it was prepared. It was found that the removal of the "wood gum" with 5 per cent sodium hydroxide did not interfere with the preparation of pergamyn. The two pulps contained equal quantities of water-soluble constituents, the pergamyn slightly less pentosans and methylpentosans than the wood pulp. He concluded that wood gum plays no part in gelatinization. The pergamyn was as resistant to acid hydrolysis, as measured by the sugar produced in a definite time, as the original pulp; hence mucilaginous carbohydrates having a lowered resistance to hydrolysis are not formed. He, accordingly, concluded that "hydration" or hydrolysis did not take place in the beater and that gelatinization was due to subdivision of the fibers into minute fibrillæ.

Schwalbe[3] found that gelatinized cellullose does show a hydrolysis difference, but to obtain definite results it is necessary that there be a wide difference in the degree of gelatinization.

Chemical wood pulp lends itself far more readily to mechanical disintegration than cotton, but has only a slight tendency to form fibrils. The coniferous fiber consists of an inner layer of spirally arranged strands and an outer layer that does not split. After prolonged beating the microscope shows the outer layer as irregular fragments, and the inner layer as a tangled mass of cloudy, gelatinous filaments.[4]

The gelatinization of cellulose by beating, according to Briggs,[5] is not a purely mechanical phenomenon but a physicochemical one. A cellulose hydrogel is formed through molecular surface distention, water being adsorbed and becoming what is now termed colloidal water. That water plays an essential part is shown by the failure of cellulose to gelatinize on beating in alcohol or petroleum. Furthermore, cellulose gelatinized by beating shows a marked reduction in the viscosity of its solutions, the viscosity decreasing with the degree of gelatinization.

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[1] J. A. de Cew, *J. Soc. Chem. Ind.*, **36** (1917), 357.

[2] H. Hofmann, *Z. angew. Chem.*, **20** (1907), 746–749.

[3] C. G. Schwalbe and E. Becker, *Z. angew. Chem.*, **32** (1919), 268.

[4] E. Kirchner, *Wochbl. Papierfabr.*, **35** (1904), 3411–3414.

[5] J. F. Briggs, *Papier-Fabr. Fest u. Auslandsheft*, **8** (1910), 46–49.

It appears that the gelatinization of cellulose by prolonged beating is accompanied and assisted by the formation of hydrocellulose and oxycellulose.[1] This is shown by the increase in reducing power. It is, in fact, possible to isolate from highly beaten pulps dextrin-like bodies having a strong reducing action on Fehling's solution.

According to Schwalbe, gelatinization increases the adsorption of copper from cold Fehling's solution, to give a high cellulose number[2]. The increase in the cellulose number is probably due more to the swelling of the incrustants than to the cellulose itself.[3] The determination of the "hydrate" copper number is satisfactory for pure cellulose but not for determining the degree of gelatinization of ground wood or raw wood pulps, since the incrustants have a reducing action on Fehling's solution.[4] According to Siebert and Minor,[5] the cellulose number of beaten wood pulps is no larger than the experimental error in the determination.

The gelatinizing capacity of wood pulps is perceptibly decreased by long boiling with water or by steaming,[6] but is increased by a preliminary treatment with acids[7] or with oxidizing agents.[8] It has been shown that the high copper number of hydrocellulose is due to the presence of dextrin-like products that can be removed by extraction with water.[9] The time required to bring a sulphite pulp of a low copper number to standard slowness by beating was reduced from 3.75 hours to 20 minutes by a preliminary trituration of the pulp in a mortar with 1 per cent hydrochloric acid.[1] Excessive acid treatment destroys the property of gelatinizing.

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[1] C. G. Schwalbe, *Z. angew. Chem.*, **32** (1919), 355.

[2] C. G. Schwalbe, "Chemie der Cellulose" (1911), 634.

[3] C. G. Schwalbe and E. Becker, *Z. angew. Chem.*, **32** (1919), 265.

[4] C. G. Schwalbe, *Papier-Fabr.*, **21** (1923), 77.

[5] F. B. Siebert and J. E. Minor, *Paper* **24,** 23 (1919), 15.

[6] C. G. Schwalbe and E. Becker, *Z. angew. Chem.*, **32** (1919), 265–269.

[7] C. G. Schwalbe, G. P., 303498 (1916); 323745 (1918); Rufferwähnt, G. P. 312179 (1918).

[8] C. G Schwalbe, G. P. 303305 (1917); 319826 (1918).

[9] O. Hauser and H. Herzfeld, *Chem. Ztg.*, **39** (1915), 689; W. Harrison, *J. Soc. Dyers Colourists*, **28** (1912), 224.

The use of oxidizing agents appears to have been anticipated by Lowe.[2] Though probably unaware of the nature of the effect produced, he recognized fully the essentials for gelatinization. The fibers were first treated with a bleach solution and then beaten with dull knives so as to have a large surface, thus pounding, instead of cutting, the fiber, "to make the stuff hold the water."

The effect of various chemicals in accelerating gelatinization, as determined by the increased bursting strength of the paper made therefrom, has been examined by Mansfield and Stephenson.[3] They used bleached sulphite pulp and a ball mill.

	Bursting strength, pounds		Bursting strength, pounds
Blank	51.5	5 per cent NH_3	73.6
1 per cent Na_2CO_3	77.4	10 per cent NH_3	84.2
3 per cent Na_2CO_3	86.0	5 per cent $ZnCl_2$	70.4
5 per cent Na_2CO_3	68.6	10 per cent NaCl	52.0
10 per cent Na_2CO_3	88.4	5 per cent H_2SO_4	51.4
5 per cent NaOH	72.2	15 per cent $CH_3.COOH$	50.6

Zinc chloride and the bases in all cases caused a marked increase in gelatinization. The acids had no effect. It is recommended that during the beating operation 1 to 5 per cent of sodium carbonate, based on the pulp, be used.

The beneficial effect of sodium carbonate and sodium hydroxide has been confirmed by Sutermeister.[4] He treated samples of steam-dried, bleached aspen soda pulp, and air-dried, bleached sulphite pulp with water and various chemicals for a period of 1 to 3 weeks. The soluble materials were then removed by washing with water and the wet pulp ground in a ball mill. In the case of the soda pulp, only water had a beneficial effect. Weak bleach solution, sodium hydroxide (2 per cent), and hydrochloric acid (2 per cent) produced a loss of strength. With the sulphite pulp, bleach solution and hydrochloric acid during the first week produced an increase in strength equal to that obtained with water, but further soaking caused a marked decrease. Calcium chloride (2 per cent), sodium chloride (5 per cent), and zinc chloride (1 per cent) caused decided increases in strength.

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[1] F. B. Siebert and J. E. Minor, *Pulp Paper Mag. Can.*, **18** (1920), 939.

[2] H. Lowe, U. S. P. 33092 (1861).

[3] E. K. Mansfield and J. N. Stephenson, *Pulp Paper Mag. Can.*, **13** (1916), 325.

[4] E. Sutermeister, *Paper* **23**, 14 (1918), 11–13.

In mucilage formation, according to Minor,[1] the first step is the production of soluble mucilaginous dextrins that are adsorbed by the pure cellulose to form the insoluble aggregate called hydrocellulose. Treatment with hot water so hastens hydrolysis and weakens adsorption that the mucilaginous products are destroyed more rapidly than formed. When triturated and non-triturated samples of parchment pulp were washed with water, the triturated sample was decidedly more alkaline to methyl red, and when washed with hot neutral water, the alkalinity increased. On washing later with cold water both pulps became acid to methyl red. Washing with hot water again developed alkalinity. This alternation of basicity and acidity could be continued for some time, indicating that acids are not produced by beating in the absence of an oxidizing agent. The theory is advanced that hydration develops more rapidly with hot water than it can be washed out, thus leaving the pulp alkaline; with cold water the reverse is true.

The addition of basic dyes to beaten wood pulps lowers their copper number.[2]

Prolonged digestion of gelatinized pulps with hot water reduces the hygroscopicity and copper number.[3] Long washing with cold water has the same effect, though not to the same extent. The pulps, in the table on page 236, before beating were given an acid treatment in accordance with G. P. 303498.

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[1] J. E. Minor, *J. Ind. Eng. Chem.*, **13** (1921), 131.

[2] F. B. Siebert and J. E. Minor, *Paper* **24** (1919), 1007.

[3] C. G. Schwalbe and E. Becker, *Z. angew. Chem.*, **33** (1920), 58–59.

Mucilage from hydrolyzed	Original mucilage			Mucilage digested with hot water 24 hours		Washed mucilage	
		Water content[1]					
	Copper number corrected	Dried at room temperature, per cent	Dried at 120°, per cent	Copper number corrected	Water content,[1] per cent	Copper number corrected	Water content,[1] per cent
Soda pulp......	11.35	37.85	25.16	3.95	16.64	8.59	26.45
Sulphite pulp...	8.59	32.65	22.95	1.03	15.11	1.69	22.65

[1] Water content in air saturated with water vapor.

It will be noted from the above table that the gelatinized pulps have a greatly increased hygroscopicity and that this is decreased by drying at 120°. Parchment paper (pergamyn) showed a reduction in hygroscopicity of 24.01 to 14.93 per cent after heating at this temperature for 2 hours. The pulp in the form of paper required an exposure of 3 to 4 weeks to water vapor to reach maximum absorption. Ordinary cellulose can be satisfied by drawing a stream of moist air over it for 5 hours. Parchment papers showing a hygroscopicity of 17.51 to 23.23 per cent had this value increased to 30.42 to 32.76 per cent by further beating.

Pulps having a high copper number, *i.e.*, retaining considerable quantities of lignin, hemicellulose, hydrocellulose, or oxycellulose, are particularly suitable for gelatinizing. It is for this reason that Mitscherlich sulphite pulp lends itself so well to the manufacture of pergamyn papers. On account of the low temperature at which this pulp is cooked, a large part of the mucilage-forming materials are retained.[1]

The ease of gelatinization of pulps varies with the species of wood, the degree and method of cooking, and the degree of bleaching. In general, for unbleached pulps, the amount of beating required increases in the order: Mitscherlich sulphite, kraft sulphate, Ritter-Kellner sulphite, soda, cotton, and mechanical wood pulp. A rough measure of ability to gelatinize may be obtained by the rattle or "tinny" character of the paper made from soda or sulphate pulps that have been cooked and beaten to the same extent. By this criterion ease of gelatinization increases in the order of the following groups of *Gymnospermæ:* (1) *Picea;* (2) *Pinus;* (3) *Pseudotsuga* (Douglas fir); (4) *Thuja, Cupressus, Chamæcyparis, Juniperus;* and (5) *Sequoia* (redwood).

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[1] C. G. Schwalbe and E. Becker, *Z. angew. Chem.*, **33** (1920), 57; C. G. Schwalbe, *Wochbl. Papierfabr* , **51** (1920), 1486; F. B. Siebert and J. E. Minor, *Pulp Paper Mag. Can.*, **18** (1920), 939.

The fibers of various species of *Prunus,* obtained by maceration of the wood in a mixture of strong nitric acid and potassium chlorate, were markedly swollen. This was not the case with various species of conifers.[1]

Action of Bacteria.—It is a common observation that celluloses gelatinized by beating undergo fermentation after standing some time, eventually losing their adhesive properties. In turn, a certain amount of bacterial action is beneficial. The fibers of *Hedychium coronarium,* after beating in a Hollander and storing in the wet condition, became more slimy and gelatinous on aging.[2] At the end of the fifth week it gave a paper having the maximum bursting strength. After the fourth week putrefaction set in, and after the fifth week gradually destroyed the material giving the paper increased strength, thus undoing the original beneficial effects of aging.

When finely divided bleached cellulose is stored under water for some time, fermentation produces a mucilaginous material.[3] The latter under suitable conditions becomes sufficiently large to permit manufacture of a paper without the addition of sizing substances. The paper on drying at 120° becomes water resistant, due to the irreversible state of the mucilage.

The degree to which pulp has been gelatinized by beating may be judged by a determination of its adsorptive capacity for sodium hydroxide in alcoholic solution,[4] and for substantive dyes, such as diamine blue and methylene blue.[3] The hygroscopic moisture method[5] gives good results with a humidity of

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[1] H. S. Conrad and W. A. Thomas, *Proc. Iowa Acad. Sci.*, **26** (1919), 333.

[2] C. Beadle and H. P. Stevens, *J. Soc. Chem. Ind.*, **32** (1913), 217–218.

[3] O. Ruff, G. P. 311772 (1918).

[4] J. F. Briggs, *Chem. Ztg.*, **34** (1910), 455.

[5] C. G. Schwalbe, *Wochbl. Papierfabr.*, **54** (1923), 22.

80 to 90 per cent. The humidity can be controlled by exposing the pulp to sulphuric acid of a definite concentration. The method is slow but accurate except when the humidity reaches the dew point.

Much ingenuity has been expended on mechanical devices to secure a rapid determination of gelatinization. Viscosity methods based on a falling sphere, flow through an orifice, or torsion,[1] are not dependable, owing to the non-homogeneity of the pulp. The apparatus in general use are based directly or indirectly on the rate of flow of water through a screen using a definite amount of pulp at a certain dilution.[2] They are generally known as sedimentation testers. The Schopper-Riegler[3] apparatus as modified by Green[4] is a very useful type.

Sedimentation tests are of questionable value unless made on the same stock.[5] Widely different chemical pulps may give identical draining values; further, the same pulp beaten under apparently the same conditions may give sedimentation curves varying widely. This variation, particularly characteristic of sulphite pulp, is probably due to lack of uniform cooking conditions.

Gelatinization of Lignocellulose.—The capability of lignocellulose to gelatinize was formerly considered to be slight.[6] According to de Cew,[7] wood does not gel as readily by mechanical treatment in the cold as does cellulose, but unlike cellulose its gelation is promoted by heat. Gelatinization has been obtained by the viscose reaction,[8] and by the limited action of strong mineral acids. Schwalbe[9] gelatinizes mechanical pulp by beating it in a Hollander in the presence of an oxidizing agent such as nitric acid.

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[1] E. W. L. Skark, *Papier-Fabr., Fest u. Auslandsheft,* **12** (1914), 87.

[2] P. Klemm, *Wochbl. Papierfabr.,* **39** (1908), 1215; E. W. L. Skark, *Papier-Fabr.,* **11** (1913), 1358, 1381, 1417; **19** (1921), 569; A. Schopper, *Papier-Ztg.,* **39** (1913), 642; "Snowshoe," *Pulp Paper Mag. Can.,* **16** (1918), 793.

[3] M. Riegler, U. S. P. 1193613 (1916).

[4] A. B. Green, *Paper* **17,** 24 (1915), 21.

[5] O. Kress and G. C. McNaughton, *Paper* **20,** 17 (1917), 13–17.

[6] C. F. Cross and E. J. Bevan, "Paper Making" (1900), p. 169; R. W. Sindall, "An Elementary Manual of Paper Technology" (1906), p. 52.

[7] J. A. de Cew, *J. Soc. Chem. Ind.,* **36** (1917), 357.

[8] P. B. Lach, E. P. 12324 (1912); Portolac Holzmasse Ges., Austrian P. 64798 (1914); J. A. de Cew, U. S. P. 1140799 (1915).

[9] C. G. Schwalbe, G. P. 303305 (1917).

The use of the Plauson colloid mill for gelatinizing cellulose and lignocellulose has been described, and alkali mentioned as a peptizing agent.[1] Three 15-liter mills in series running at 9000 r.p.m. will in 1 hour reduce 200 kilograms of cellulose to such fineness that 85 per cent of the particles will be about 0.001 millimeter in diameter.[2] The power consumption, 15 to 20 kilowatts per kilogram of substance, is very high.[3]

It was found that by grinding wood in water in a ball mill for 24 to 48 hours the conifers could be readily gelatinized, but the hardwoods showed little change; however, the addition of sufficient sodium hydroxide to form a 0.25 per cent solution had a marked peptizing action, particularly on the hardwoods.[4] The reaction has been applied to the bark of trees and the cereal straws. The higher the hemicellulose content of a substance, the more readily it gelatinizes. With iodine solution, gelatinized wood stains blue, like cellulose. In the dry condition it forms a dense, horn-like mass having a specific gravity of 1.5. When dry wood was ground in a solution of sodium hydroxide in absolute methyl alcohol, then filtered and washed with alcohol, the residue on drying formed an easily friable mass that remained unaffected by water; however, when water was used for washing the wood while still wet with alcohol, it became gelatinous at once. This indicates that gelatinization takes place in two stages: the wood first acquires by mechanical comminution a peculiar affinity for water with which it then combines to form a gelatinous product.

It does not appear to be possible to produce gelatinization by either mechanical or chemical methods without destroying the regular orientation of the crystallites or micellæ about the axis of the fiber. Straight pressures of 500,000 pounds to the square inch applied to wood and chemical pulp in either the air-dry condition, or wet with water or dilute sodium hydroxide, did not produce gelatinization.[1] Microscopic examination indicated no visible disintegration of the fibers. More promising results are obtained with calenders where there is a certain shearing action. The effect of mechanical disintegration on cellulose is a field worthy of further investigation. Either dry or wet beating results in a decrease in the viscosity of the cuprammonium solutions of the cellulose so treated.[2] The mechanical disintegration of cellulose by beetling results in a chalky powder that no longer stains blue with iodine solution.[3] Tests for oxycellulose and hydrocellulose were negative. Treatment with 17.5 per cent sodium hydroxide showed 44.2 per cent α-cellulose, 48.6 per cent β-cellulose, and 7.2 per cent γ-cellulose.[4] The yield of acetate on acetylation was 122 per cent in comparison with 178 per cent for normal cellulose. When heated in water above 77°, the suspended cellulose underwent an apparent hydration effect, the powder changing to a flocculent curd. The phenomenon was reversible, a powder being obtained on cooling.

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[1] B. Block, *Z. angew. Chem.*, **34** (1921), 28; *cf.* H. Plauson, *Chem. Ztg.*, **44** (1920), 535, 565; *Z. angew. Chem.*, **34** (1921), 469, 473; A. W. Kenney, *Chem. Met. Eng.*, **27** (1922), 1080.

[2] A. Forster and J. Reilley, *J. Soc. Chem. Ind.*, **41** (1922), 438R.

[3] W. J. Kelley, *J. Ind. Eng. Chem.*, **15** (1923), 926.

[4] A. W. Schorger, *J. Ind. Eng. Chem.*, **15** (1923), 812.

Cellulose Solvents. Cuprammonium Solution.—There is no true solvent for cellulose. The various so-called solvents permit the recovery of a modified cellulose only. On dilution of the solvent, gelatinous cellulose usually precipitates. The extent to which the cellulose is degraded depends upon the nature of the solvent and the length of time that the cellulose remains in the solvent.

Schweizer's reagent,[5] an ammonical solution of cupric oxide,

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[1] Unpublished results.

[2] P. Waentig, *Text. Forsch.*, **3** (1921), 154.

[3] M. Fort, *J. Soc. Dyers Colourists*, **34** (1918), 9–10.

[4] C. F. Cross and E. J. Bevan, *J. Soc. Dyers Colourists*, **34** (1918), 215–218.

[5] E. Schweizer, *J. prakt. Chem.*, **72** (1857), 109; **78** (1859), 370.

The discovery of the solvent action of cuprammonium solution is invariably attributed to Schweizer, usually incorrectly spelled Schweitzer in the literature. E. A. Parnell, in "Life and Labours of John Mercer," London (1886), p. 214, states: "Mercer appears to have been the first to notice the remarkable action which the ammoniacal solution of cupric oxide exerts on cotton fibre. He found that cotton is completely soluble in the liquid obtained by dissolving hydrated cupric oxide to saturation in ammonia of sp. gr. 0.920 and diluting with three measures of water. On neutralizing this solution with sulphuric acid, the organic matter was precipitated, and dissolves cellulose rapidly. Its solvent power is very limited.[1] After treatment with an excess of cotton for a few minutes, the cuprammonium solution not only loses its ability to dissolve more cotton, but fresh cotton is not even swelled by it. The solvent power is greatly reduced or prohibited by the presence of salts.[2]

Ammoniacal nickel oxide does not attack cellulose.[3]

Gibson,[4] following Dawson's[5] method for preparing crystalline cupric hydroxide, prepares the cuprammonium solution as follows: 60 grams of copper sulphate are dissolved in 1 liter of hot water and a few drops of sulphuric acid added. The solution is cooled to 50° and ammonia of sp. gr. 0.880 is added until the precipitation of basic copper sulphate is complete, any excess of ammonia being neutralized with a few drops of sulphuric acid. After settling and decanting, the precipitate is washed with hot water by decantation, 200 cubic centimeters of 20 per cent sodium hydroxide added, and the whole shaken at the ordinary temperature. The precipitate is washed with cold water by decantation until it is free from alkali and salts. It is then collected on a porous plate and dried at 40°. The dried product is transferred to an aspirator bottle, 800 cubic centimeters of ammonia water containing 200 to 210 grams of ammonia per liter added, and the whole well shaken. The excess cupric hydroxide is allowed to settle. The solution is then filtered through glass wool. When used for viscosity measurements, the amount of copper present is determined and sufficient ammonia is added to give a solution containing 11 grams of copper and 200 to 210 grams of ammonia per liter.

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the latter became free from copper by an excess of sulphuric acid." Mercer recognized that a low temperature and absence of salts increased the solvent power of the solution. A solution prepared in accordance with the above would have a low solvent power. Why he diluted with water is not apparent.

The date of these discoveries is not stated. Mercer was born Feb. 21, 1791 and died Nov. 30, 1866.

[1] C. Cramer, *J. prakt. Chem.*, **73** (1858), 7.

[2] J. Schlossberger, *Ann.*, **107** (1858), 23.

[3] J. Schlossberger, *l.c.*, 21.

[4] W. H. Gibson, *J. Chem. Soc.*, **117** (1920), 492.

[5] H. M. Dawson, *J. Chem. Soc.*, **95** (1909), 371.

The cuprammonium solution prepared from basic copper sulphate by Ost's[1] method contains tetrammine copper sulphate.[2]

Joyner[3] prepared the reagent by bubbling air through a mixture of copper turnings in strong ammonia, a little sucrose being added to hasten solution of the copper. In this way it is possible to prepare solutions containing more than 30 grams of copper per liter. This method has been used industrially.[4] A solution containing 40 to 50 grams of copper per liter can be prepared by means of compressed air and low temperatures.[5]

Mulder[6] prepared solutions of cellulose by repassing ammonia through alternate layers of copper turnings and cotton in a separatory funnel.

It has been stated[7] that an ammoniacal solution of cuprous chloride dissolves cellulose rapidly; in the absence of oxygen, however, no solution takes place.[8] A solution prepared by treating 90 grams of copper oxychloride with 850 to 900 cubic centimeters of ammonia water of sp. gr. 0.93 will dissolve 100 grams of cellulose.[9] In this case, the presence of chlorides is assumed to be beneficial.

Primary aliphatic diamines saturated with cupric hydroxide have the property of dissolving cellulose to a marked extent, being superior in this respect to equal concentrations of ammonia.[10] With ethylene diamine there is formed the compound $Cu(C_2H_8N_2)_2.(OH)_2$. Solutions containing as little as 2 to 8 per cent of ethylene diamine are effective as solvents. Cellulose is only slightly soluble in corresponding aqueous solutions of primary aliphatic amines and insoluble in secondary.

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[1] H. Ost, *Z. angew. Chem.*, **24** (1911), 1893.

[2] W. H. Gibson, *l.c.*

[3] R. A. Joyner, *J. Chem. Soc.*, **121** (1922), 1511.

[4] E. Bronnert, M. Fremery, and J. Urban, G. P. 115989 (1900).

[5] C. Süvern, "Die Küntsliche Seide," p. 100.

[6] E. Mulder, *Jahresber. Chemie*, (1863), 566.

[7] M. Rosenfeld, *Ber.*, **12** (1879), 956.

[8] C. F. Cross and E. J. Bevan, "Cellulose" (1895), p. 246.

[9] R. Pawlikowski, F. P. 403488 (1909).

[10] W. Traube, *Ber.*, **44** (1911), 3319; G. P. 245575 (1911); E. Friedrich, U. S. P. 850571 (1907).

The solvent power of cuprammonium solutions is greatly increased by the presence of sodium hydroxide.[1] The solubility of cupric hydroxide in the caustic alkalis alone is slight. One liter of sodium hydroxide of sp. gr. 1.345 to 1.370, or potassium hydroxide of sp. gr. 1.453 to 1.498, will dissolve about 7.8 grams of copper hydroxide.[2]

When cellulose is treated with a fixed alkali, an alcoholate is apparently formed. This reacts with cupric hydroxide to form an alkali-copper-alcoholate.[3] The fixed alkali may be replaced by metallic ammonium hydroxides. Cellulose forms with Schweizer's reagent an alcoholate, the hydrogen of the free hydroxyl groups being replaced by copper to give a salt as follows:

$$[Cu(NH_3)_4](OH)_2 + \underset{\text{Cellulose}}{[HO{\cdot}C_6H_7O_2(OH)_2]_2} \longrightarrow \underset{(A)}{[Cu(NH_3)_4]\cdot[O{\cdot}C_6H_7O_2(OH)_2]_2} + 2H_2O$$

$$(A) + Cu(OH)_2 \longrightarrow [Cu(NH_3)_4]\cdot[O{\cdot}C_6H_7O_2(OH)O]_2\,Cu + 2H_2O.$$

According to Hess,[4] the compound $[Cu(NH_3)_4]\cdot[C_6H_7O_5Cu]_2$ is formed.

Caustic soda coagulates a cuprammonium solution of cellulose, forming a transparent, blue copper-alkali compound[5] of the composition $Na_2(C_{12}H_{16}O_{10})Cu$.

Wood cellulose was dissolved in a solution of copper carbonate in ammonia. On heating this solution there was deposited a copper-cellulose compound considered[6] as having the definite composition $11CuO{\cdot}2C_6H_{10}O_5{\cdot}2H_2O$.

Metallic zinc gradually removes all the copper from cuprammonium solutions of cellulose, giving a colorless liquid having properties similar to the copper compound.[1] Some cellulose usually separates during the treatment.

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[1] M. Prud'homme, F. P. 344138; P. Friedrich, F. P. 410882 (1909).

[2] E. Justin-Mueller, *Compt. rend.*, **167** (1918), 779.

[3] W. Traube, *Ber.*, **54B** (1921), 3220; **55B** (1922), 1899; **56B** (1923), 268.

[4] K. Hess *et al.*, *Ann.*, **435** (1923), 1.

[5] W. Normann, *Chem. Ztg.*, **30** (1906), 584; K. Hess *et al.*, *Ber.*, **55B.** (1922), 2432; **56B** (1923), 587.

[6] H. Riesenfeld and F. Taurke, *Ber.*, **38** (1905), 2798.

The keeping quality of cuprammonium solutions of cellulose is improved by the addition of mannitol and other polyatomic alcohols.[2]

Sodium chloride, and various other salts, precipitate cellulose from the solution. The precipitated cellulose is colored violet to wine red by tincture of iodine.[3] Besides salts, the cellulose is precipitated by acids, even carbonic acid, and sugar.[4]

Strong ammonia added to copper sulphate forms tetrammine copper hydroxide,[5] $Cu(NH_3)_4.(OH)_2$. The ions Cu_nNH_3'' and Cu'' are also present.[6]

In general, the higher the percentage of copper in Schweizer's reagent the greater is its solvent power. Grimaux,[7] as a result of experiments on dialysis, concluded that it was the non-dialyzable portion that acted as a solvent. According to Connerade,[8] the solubility of cellulose is proportional to the concentration of the colloidal cuprammonium hydroxide, the concentration being greater for solutions prepared at low temperatures. The fixation of copper follows the adsorption laws, though there are no stoichiometrical relations between the weight of cuprammonium hydroxide and the weight of the cellulose. This is due to solution of cellulose being a colloidal phenomenon.[9] The colloidal portion of the cuprammonium hydroxide combines with the cellulose to give an adsorption compound soluble in ammonia. Cuprammonium solutions have almost the same tension of ammonia as solutions of ammonia of equal concentration; hence colloidal copper hydroxide must be present, though it plays a secondary rôle in the solution of the cellulose. The presence of cellulose in solution does not change the ammonia tension. Dialysis gives a product containing 69.5 per cent cellulose and 30.5 per cent copper hydroxide.

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[1] E. Mulder, *Jahresber. Chemie,* (1863), 566.

[2] P. Friedrich, F. P. 400321 (1909).

[3] J. Schlossberger, *Ann.,* **110** (1859), 247.

[4] E. Mulder, *Jahresber. Chemie.* (1863), 566.

[5] J. Locke and J. Forssall, *Am. Chem. J.,* **31** (1904), 268.

[6] H. M. Dawson, *J. Chem. Soc.,* **89** (1906), 1666.

[7] E. Grimaux, *Compt. rend.,* **98** (1884), 1434.

[8] E. Connerade, *Bull. soc. chim. Belg.,* **28** (1914), 176; *cf.* Soc. Anon. Crinoid F. P. 401741 (1908); U. S. P. 947715 (1910).

[9] E. Berl and A. G. Innes, *Z. angew. Chem.,* **23** (1910), 987.

The solubility of cellulose in a cuprammonium solution depends not only on the solution itself but on the condition of the cellulose. Cellulose dissolves almost immediately if it has been mercerized with caustic soda.[1] Obviously, the cellulose should be free from fats and waxes. The cuticle of cotton is insoluble and offers mechanical resistance (Fig. 6) to the solution of the fiber; hence the use of bleaching agents, such as calcium hypochlorite, that destroy the cuticle, greatly facilitates solution.[2]

Statements regarding the solubility of cellulose accordingly vary greatly. A solution containing 150 to 200 grams of ammonia and 18 grams of copper per liter, prepared by drawing air through ammonia in contact with copper, dissolved 3 per cent of cellulose. The solubility of cellulose based on the copper present is stated to be as follows:

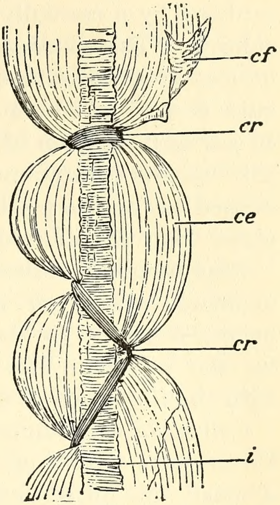

Fig. 6.—Cotton swollen in cuprammonium solution. *cf*, shreds of cuticle; *cr*, ring of cuticle; *ce*, distended cellulose; *i*, dried protoplasmic lining of the banded lumen, greatly shrunken and hence wrinkled transversely. (*After von Höhnel.*)

Cellulose Dissolved by 1 Part of Copper	
2	R. Pawlikowski, F. P. 403488 (1909).
2.5	P. Friedrich, F. P. 410882 (1909).
3	H. Pauly, G. P. 98642 (1897).
2.3	R. A. Joyner, *J. Chem. Soc.*, **121** (1922), 1511.

According to Pauly, the solution contained 45 grams of cellulose per liter, or approximately 4.5 per cent. Fremery and Urban[3] obtained a 4 per cent solution with ordinary cotton.

Cellulose dissolved in cuprammonium solution is used in the manufacture of Pauly silk (Glanzstoff). The solution should contain at least 5 per cent of cellulose, preferably 8 to 10 per cent.[1] To obtain solutions of these concentrations, it is necessary to use a cellulose that has been mercerized or slightly oxidized by a carefully regulated treatment with calcium hypochlorite. The solution, after filtering, is spun through capillary orifices at a pressure of 2 to 4 atmospheres. The coagulating bath is a 45 to 50 per cent solution of suphuric acid or a 30 to 40 per cent solution of sodium hydroxide. The manufacture of silk by the cuprammonium process is expensive but is still carried on, as the product has a somewhat greater resistance to water than the other kinds of artificial silks.

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[1] E. Thiele, *Rev. prod. chim.*, **3** (1900), 325.

[2] M. Fremery and J. Urban, G. P. 111313 (1899).

[3] M. Fremery and J. Urban, *l.c.*

Prud'homme[2] states that cuprammonium solution has an oxidizing action on cellulose similar to hydrogen peroxide; hence, contrary to the general opinion, cellulose is attacked by the solvent. The ammonia likewise undergoes oxidation with the formation of nitrites.

Cellulose cuprammonium solutions are of slight stability. Precautions should be taken to guard them from air and light. A small amount of oxygen has an enormous effect on the viscosity. Joyner[3] believes that there are two kinds of cellulose: "A" having a maximum viscosity of 57,000 seconds for a 2 per cent solution at 20°; "B" having the low viscosity of a second for a 5 per cent solution. Sixteen grams of oxygen will react with about 2,100 grams of cellulose, converting all of "A" into "B." When cellulose, in a caustic soda solution, was treated with 1.5 cubic centimeters of sodium hypochlorite per gram, the viscosity of a 4 per cent solution in cuprammonium was reduced to 4 seconds.

The viscosity of the solution affords a useful means, when stringent precautions are observed,[4] of determining if the cellulose is normal or degraded.[5] Joyner[6] recommends for general use, a solution of 20 grams of cellulose in a reagent containing 13 grams of copper and 200 grams of ammonia per liter. In the case of a cellulose of low viscosity, 40 grams of the product are dissolved in a reagent containing 20 grams of copper and 200 grams of ammonia per liter.

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[1] Ullmann, "Enzyklop. tech. Chemie," **7** (1919), 330.

[2] M. Prud'homme, *Compt. rend.*, **112** (1891), 1374.

[3] R. A. Joyner, *J. Chem. Soc.*, **121** (1922), 2395.

[4] W. H. Gibson, *J. Chem. Soc.*, **117** (1920), 479; M. Nakano, *J. Chem. Ind.* (*Japan*), **25** (1922), 899; R. A. Joyner, *l.c.*

[5] C. Piest, *Z. angew. Chem.*, **25** (1912), 2518; H. Ost, *Ibid.*, **24** (1911), 1892.

[6] R. A. Joyner, *J. Chem. Soc.*, **121** (1922), 1511.

Changes in the viscosity of the solution, attributed to depolymerization of the cellulose molecule, show that the solvent is not inert and prevents sharp differentiation between celluloses. Ost[1] obtained the highest viscosity for a nitration cotton that had been boiled with dilute caustic soda. The lowest viscosities and easiest solubilities were shown by filter paper and bleached straw cellulose. Sulphite pulp purified for celluloid manufacture showed a viscosity of 10.7°. The viscosity of cotton was reduced from 30.2 to 13.6° by a previous heating at 120 to 125° for 15 hours. Oxycellulose and hydrocellulose show a low viscosity. The residues from heating these degraded celluloses with alkalis is usually considered as pure cellulose; yet they still show low viscosities.

Nakano[2] found the following changes in the viscosity of cellulose (S. S. filter paper No. 590) after heating for 4 hours at various temperatures:

Temperature.....	Control	100–105°	120–125°	140–145°	160–165°	180–185°
Viscosity.........	2.26	2.20	2.14	1.87	1.62	1.51

Cotton, 10 grams, mercerized with 200 cubic centimeters of sodium hydroxide solutions for 24 hours, showed the following viscosities:

NaOH, per cent....................	Control	11	17	20
Viscosity..........................	4.22	3.59	3.03	2.01

Depolymerization of the molecular cellulose aggregate, other conditions being equal, is due to light.

Crystallization of Cellulose.—In 1893, Gilson[3] reported that cellulose could be obtained in the form of crystals. Cotton and thin sections of plants were treated with Schweizer's reagent. After becoming strongly swollen, the cellulose was treated with ammonia until the preparation was almost colorless. This was followed by water, and dilute hydrochloric acid or acetic acid. With proper precautions the cellulose was converted into a mass of isotropic spherocrystals. Crystals were obtained from the wood of two species of gymnosperms and from the celluloses from various species. The crystals were insoluble in boiling 2 per cent sulphuric acid and, since they were without action on polarized light, they are to be considered as crystallites rather than crystals.

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[1] H. Ost, *l.c.*

[2] M. Nakano, *l.c.*

[3] E. Gilson, *La Cellule*, **9** (1893), 397–440.

Gilson's findings were confirmed by Johnson[1] and Bütchli.[2] De Mosenthal[3] identified the crystals microchemically as cuprous chloride. He states that when acetic acid is used no crystals are obtained.

According to the more recent investigations of Alexandrowicz,[4] spherocrystals of cellulose can be obtained in a few hours by immersing in concentrated ammonia a capillary tube containing a dilute solution of cellulose in cuprammonia. The crystals lose their structure on complete drying. While the cellulose of plants is strongly doubly refractive, the cellulose crystals are isotropic or very weakly anisotropic. Hemicelluloses increase the optical anisitropy of cell tissues.

Salts as Cellulose Solvents.—A sheet of paper plunged into a hot, concentrated solution of zinc chloride swells and dissolves without coloration.[5] Before undergoing saccharification the cellulose passes through a stage in which it is stained blue by iodine. When cotton is moistened with about 10 parts of 40 per cent zinc chloride solution, and the mixture gradually warmed to the temperature of a hot water bath, a syrupy solution is finally obtained.[6] Water precipitates gelatinized cellulose containing 18 to 25 per cent of zinc oxide that can be removed by treatment with dilute hydrochloric acid and washing.

The solutions of cellulose obtained with zinc salts have been used for producing threads and filaments, but its use for these purposes has practically disappeared, as the solvent has a destructive action on the cellulose. The solvents consisted of zinc chloride, bromide, or iodide; or bismuth chloride or bromide separately or as mixtures;[1] and zinc chloride with 5 per cent of a suitable alkaline earth chloride such as calcium chloride.[2] As with other solvents, the cotton is dissolved more readily and gives more concentrated solutions if previously mercerized or converted to hydrocellulose.

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[1] D. S. Johnson, *Botan. Gaz.*, **20** (1895), 16–22.

[2] O. Bütchli, "Untersuchungen über Strukturen," Leipzig (1898), p. 200.

[3] H. de Mosenthal, *J. Soc. Chem. Ind.*, **23** (1904), 293.

[4] J. S. Alexandrowicz, *Arch. ges. Physiol.*, **150** (1913), 57–86.

[5] C. Barreswil, *J. pharm. chim.*, **21** (1852), 205.

[6] C. F. Cross and E. J. Bevan, "Cellulose," p. 8.

It has been observed by Deming[3] that numerous metallic salts having an acid reaction in aqueous solution are capable of dissolving cellulose. A pyridine or quinoline solution of zinc chloride will not dissolve normal cellulose even on heating. Their solvent power is greatly increased by the addition of strong hydrochloric acid. Four parts of stannous chloride dissolved in one part of water will dissolve cellulose at 100°, while the solution of the salt in concentrated hydrochloric acid will dissolve it in the cold.

When dissolved in strong hydrochloric acid, the solvent powers of the various salts were:

Solvent power	Salt
Good	$SbCl_3$, $SbCl_5$, $HgCl_2$, $BiCl_3$, $SnCl_4$, $TiCl_4$
Moderate	$CoCl_2$, $AuCl_3$, UO_2Cl_2, $CeCl_3$, $CrCl_3$
Poor	$CdCl_2$, Cu_2Cl_2, $TlCl_3$, VCl_4
None	$MnCl_2$, $CuCl_2$, $NiCl_2$, $AgCl$, $PbCl_2$, $TlCl$, $AlCl_3$, $ThCl_4$, $AsCl_3$

Solutions of chlorides of the alkalis and alkaline earths in hydrochloric acid do not dissolve cellulose, owing probably to their slight solubility in this medium; however, solutions of $CaCl_2$, $CaBr_2$, $BaCl_2$, $MgBr_2$, $LiCl$, and KBr in formic acid, alone or admixed with hydrochloric acid, do dissolve cellulose.

Ferric chloride, $FeCl_3.6H_2O$, in the molten condition dissolves cellulose rapidly.

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[1] J. Wynne and L. Powell, E. P. 16805 (1884).

[2] W. P. Dreaper and H. Tompkins, E. P. 17901 (1897).

[3] H. G. Deming, *J. Am. Chem. Soc.*, **33** (1911), 1515–1525.

In 1905, Dubosc[1] accidentally discovered that some thiocyante solutions, especially when heated, were cellulose solvents giving solutions adapted to spinning. Solution was attributed to the formation of a cellulose thiocyanic ester. Dubosc used the ammonium, potassium, calcium, and iron salts. Potassium thiocyanate[2] melted with a few drops of water will dissolve cellulose at 200°. Any soluble thiocyanate will also dissolve alkali-cellulose.[3]

The action of the thiocyanates has been carefully examined by Williams.[4] It was found that, in the case of a neutral salt, there is a definite connection between the boiling point, viscosity, and heat of dilution of its solution and its ability to dissolve cellulose. These properties must be brought within definite limits. None of the thiocyanate solutions dissolved cellulose until the boiling point of the solution reached 133 to 134°. There must be a positive heat of dilution not exceeding about 3500 calories, and the viscosity must be at least 3.3 times that of water at 20°.

Lithium thiocyanate does not dissolve cellulose until its solution is concentrated to a boiling point of 165°, where the proper viscosity is reached; but when the viscosity is increased by the addition of compounds that increase the viscosity without diminishing the heat of dilution, a solvent can be obtained having a boiling point 30° lower. The addition need not be a thiocyanate for thiourea or dicyandiamide may be used. In this way, thiocyanates not in themselves solvents can be made active by the proper addition of other thiocyanates or compounds.

Calcium thiocyanate is the best solvent. A solution boiling at 133° will dissolve wood pulp by heating to 90°. The solution must be neutral or acid; if alkaline, no solution takes place. A little acetic acid assists solution. The addition of 1 volume of calcium chloride solution, b.p. 133°, to 2 volumes of calcium thiocyanate solution, b.p. 133°, does not decrease the solvent power of the latter. With solutions of b.p. 140°, equal volumes of the two solutions may be used. One hundred cubic centimeters of the mixture will dissolve 7 grams of cotton or wood pulp. Unlike sulphuric acid, this solution can be used for parchmentizing paper containing lignocellulose. It can be used for making vulcanized fiber and in spinning threads, coagulation taking place in 50 to 90 per cent alcohol.

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[1] A. Dubosc, *Bull. Rouen*, **33** (1905), 318; *Rev. prod. chim.*, **26** (1923), 507.

[2] H. G. Deming, *l.c.*, 1523.

[3] A. Dubosc, *Bull. Rouen*, **36** (1908), 272.

[4] H. E. Williams, *J. Soc. Chem. Ind.*, **40** (1921); 221T; *Mem. Proc. Manchester Lit. Phil. Soc.*, **65**(1921), 12; *cf.* U.S.P. 1301652; E.P. 123784 (1917).

While it might be assumed that cellulose would undergo but slight degradation in a neutral solvent, this does not appear to be the case. Beck[1] dissolved cellulose in a concentrated solution of calcium thiocyanate at 120°. The solution set to a clear jelly on cooling. Films prepared from the solution had less strength than for cellulose prepared from viscose or a cuprammonium solution. It was found that the strength of the films could be increased 80 per cent in both the wet and dry condition by immersion in a concentrated solution of calcium thiocyanate at room temperature for 24 hours. The strength of the film was greater also if the calcium thiocyanate was not completely removed by washing.

An interesting theory of the solvent action of neutral salt solutions on cellulose has been given by Williams.[2] The hydroxyl groups of the cellulose unit combine with the salt complex in place of water molecules, behaving as a substituted water group, thus causing the fiber to swell considerably. In this way the cellulose unit is brought into molecular range with the water molecules combined with the salt. By raising the temperature, the union between the salt and water molecules will weaken and tend to part from the parent molecule. The water thus freed migrates to the cellulose by which it is imbibed, causing further swelling of the fiber, which increases as the progressive hydration proceeds. The highly swollen fiber in the gelatinous condition then peptizes, and passes into colloidal solution.

Octacetylcellobiose and pentacetylglucose dissolve in solutions of calcium thiocyanate, bromide, and chloride without saponification.[3] Cellulose nitrate can also be swollen in solutions of calcium thiocyanate or chloride without noticeable decomposition. Cellulose formate dissolves readily in a 20 per cent solution of the thiocyanates.[1] According to Dubosc,[2] this is not a case of simple solution but a double decomposition with the formation of a cellulose thiocyanic ester.

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[1] F. Beck, *Z. angew. Chem.*, **34** (1921), 113.

[2] H. E. Williams, *l.c.*

[3] K. Schweiger, *Z. physiol. Chem.*, **117** (1921), 65.

Hydrogen Peroxide as a Cellulose Solvent.—Cellulose and its modifications are soluble in hydrogen peroxide of a concentration of 60 per cent or greater.[3] Swelling first takes place followed by solution. Addition of water to the viscous solution precipitates the cellulose in a chemically changed form. The more modified the original cellulose, the more readily it dissolves. Treatment of cellulose with alkalis increases the solubility, so that hydrogen peroxide is suggested as a suitable reagent for detecting mercerization.

Acids as Cellulose Solvents.—Concentrated sulphuric and hydrochloric acids dissolve cellulose, first transforming it into a swollen gelatinous mass.[4] Béchamp[5] states that the hydrochloric acid used had a sp. gr. of 1.20 (39.8 per cent). Pelouze[6] observed that concentrated hydrochloric acid is an excellent solvent for cellulose. If the latter is precipitated with water a short time after solution, it resembles the cellulose obtained from cuprammonium solutions. After a day or two, a precipitate is no longer obtained and the solution strongly reduces Fehling's solution.

Cellulose that has been precipitated from a cuprammonium solution will dissolve in hydrochloric acid of a concentration not effecting solution of the ordinary forms of cellulose.[7]

The solvent power of hydrochloric acid has been studied in detail by Willstätter and Zechmeister.[8] Acid containing 37.6 per cent of hydrogen chloride, after contact with cellulose for one day, causes disintegration and gelatinization. Solution does not take place in acid of sp. gr. 1.196 (about 39.2 per cent).[1] The most suitable concentrations are 40 to 42 per cent. On shaking cellulose at room temperature with acid of 40.8 per cent, a clear solution is obtained in 10 seconds. Acids of a concentration of 39.9, 40.8, and 41.4 per cent will dissolve 7, 12 to 13, and 15 per cent of cellulose, respectively. If water is added to the solutions during the first 30 to 45 minutes, the cellulose is quantitatively precipitated.

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[1] C. F. Cross and E. J. Bevan, *J. Chem. Soc.*, **99** (1911), 1450.

[2] A. Dubosc, *Caoutchouc and gutta-percha*, **10** (1913), 6895.

[3] M. Bamberger and J. Nussbaum, *Monatsh.*, **40** (1919), 411.

[4] A. Béchamp, *Compt. rend.*, **42** (1856), 1213.

[5] A. Béchamp, *Compt. rend.*, **100** (1885), 370.

[6] J. Pelouze, *Compt. rend.*, **48** (1859), 327.

[7] J. Pelouze, *Compt. rend.*, **48** (1859), 210.

[8] R. Willstätter and L. Zechmeister, *Ber.*, **46** (1913), 2995; L. Zechmeister, Diss. Zürich (1913); R. Willstätter, G. P. 273800 (1913).

Hydrobromic acid of a concentration of 48 per cent gelatinizes cellulose. The latter is dissolved completely by 57 per cent acid at room temperature, and by 66 per cent acid at 0°.

Concentrated hydriodic acid does not dissolve cellulose in the cold.

Hydrofluoric acid of a concentration of 70 to 75 per cent gelatinizes and dissolves cellulose rapidly.[2]

The reputed solvent power of chloral hydrate[3] is probably due to hydrochloric acid formed by decomposition. In the presence of chloral hydrate and concentrated sulphuric acid, cellulose gives dichloralglucoses.[4]

Sulphuric acid of a concentration of 70 to 75 per cent is most suitable for dissolving cellulose. The 80 per cent acid soon produces charring. While 60 per cent acid gelatinizes cellulose, it will not dissolve it at room temperature during 3 weeks.[5]

Numerous mixtures and concentrations of acids have been employed for dissolving cellulose for the production of filaments as well as for saccharification. There may be mentioned: concentrated sulphuric acid;[6] a mixture of sulphuric and phosphoric acids;[7] a mixture of hydrochloric and sulphuric or phosphoric acids;[8] and glacial acetic and phosphoric acids.[9]

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[1] Ferguson's table; only 38.35 per cent by that of Lunge and Marchlewski.

[2] L. Zechmeister, *l.c.*, 38.

[3] T. A. Edison, *Chem. News*, **36** (1877), 138.

[4] J. H. Ross and J. M. Payne, *J. Am. Chem. Soc.*, **45** (1923), 2363.

[5] H. Mühlmeister, Diss. Hannover. (1913), p. 21.

[6] R. Langhans, G. P. 72572 (1891).

[7] R. Langhans, G. P. 82857 (1893).

[8] Z. Ostenberg, U. S. P. 1218954 and 1242030 (1917); 1315393 (1919); 1348731 (1920); International Cellulose Co. F. P. 484442 (1917); V. Hottenroth, Danish P. 23957 (1918); Swiss P. 76329 (1917).

[9] K. H. Hofmann, G. P. 227198 (1909).

Berl[1] dissolves cellulose in 60 to 77 per cent sulphuric acid at a temperature not above −10° to obtain a solution suitable for films and artificial silk.

Cellulose dissolves instantly in a solution of zinc chloride in twice its weight of concentrated hydrochloric acid.[2] A solution of zinc chloride in two parts of acetic anhydride gelatinizes cellulose but does not dissolve it even on heating.[3] In this case, acetylcellulose is formed.

Arsenic acid slowly dissolves cellulose in the cold, solution being hastened by heating.[4] Selenic acid shows a slight solvent action on heating.

Viscose.—In 1893, Cross and Bevan[5] published their discovery of the viscose reaction. They found that when cellulose was impregnated with a mercerizing solution of caustic soda, and carbon bisulphide then added, a water-soluble sodium salt of cellulose xanthogenic acid or thiocarbonic acid was obtained. This salt, called viscose, could be readily decomposed with the formation of a gelatinized cellulose. The regenerated cellulose was known as viscoid, though today the term is generally supplanted by viscose.

Cellulose can be gelatinized by the thiocarbonate reaction, and yet left insoluble in water, by using caustic soda of a strength insufficient to produce mercerization.[6] Cotton is treated with 2.5 to 3 parts of 9 per cent sodium hydroxide and 15 per cent of carbon bisuphide. On the addition of water, the fibers swell in proportion to the ratio of alkali to cellulose employed, and the temperature at which the alkali reacts with the cellulose. De Cew[7] adds carbon bisulphide to cellulose that has absorbed approximately 2 per cent by weight of alkali.

Theoretically, during the viscose reaction, sodium cellulose xanthogenate is formed as follows:

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[1] E. Berl, G. P. 259248 (1912).

[2] C. F. Cross and E. J. Bevan, *Chem. News*, **63** (1891), 66.

[3] T. F. Hanausek, *Chem. Ztg.*, **18** (1894), 441.

[4] H. G. Deming, *J. Am. Chem. Soc.*, **33** (1911), 1523.

[5] C. F. Cross, E. J. Bevan, and C. Beadle, *Ber.*, **26** (1893), 1090; E. P. 8700 (1892); U. S. P. 520770 (1894).

[6] C. F. Cross and E. J. Bevan, E. P. 126174 (1918).

[7] J. A. de Cew, U. S. P. 1140799 (1915).

$$(C_6H_{10}O_5)_x + xNaOH = (C_6H_9O_4.ONa)_x + xH_2O.$$

$$C_6H_9O_4.ONa + CS_2 = C_6H_9O_4.O.CS.SNa.$$

Sodium cellulose
xanthogenate

In practice, it was found necessary to use twice the theoretical amount of sodium hydroxide in order to obtain a soluble product. This phenomenon, coupled with the inability of the authors[1] to obtain higher than a dibenzoyl derivative of cellulose by the Baumann reaction, led them to suppose that two hydroxyl groups in the cellulose reacted with or were influenced by the alkali.

Cellulose xanthogenic acid is a comparatively strong acid and its salts are not decomposed by weak organic acids. By titrating first with acetic acid, then with a mineral acid, only one sodium atom can be accounted for in each C_6 group. The same result is obtained by titrating, with iodine, pure sodium cellulose xanthogenate isolated by neutral dehydrating agents.

$$2RO.CS.SNa + 2I = RO.CS.S\text{-}S.CS.OR + 2NaI$$

The viscose solution decomposes spontaneously on standing, with the setting free of gelatinized cellulose. During this transition, three fairly well-defined stages can be observed. The maximum degree of reaction gives the C_6 xanthogenate, $C_6H_9O_4.O.CS.SNa$. The cellulose residue, in reality, lies between C_6 and C_{12}, since no sharp line of demarcation exists. The compound is not precipitated from the freshly prepared solutions by dehydrating agents. After about 24 hours, it reverts to the C_{12} xanthogenate that can be precipitated by such reagents as alcohol and salt, and redissolved in water. In the absence of an excess of alkali, the viscose solution changes in 6 to 10 days to the C_{24} xanthogenate. It is soluble in alkaline solution but insoluble in water, since it is completely precipitated by acetic acid; hence the solubility is due to a reaction between the alkali and the hydroxyl groups of the cellulose.[2]

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[1] C. F. Cross, E. J. Bevan, and J. F. Briggs, *Ber.*, **34** (1901), 1513.

[2] C. F. Cross and E. J. Bevan, "Cellulose" (1916), p. 318.

Ost[1] found that in freshly prepared viscose, two atoms of sulphur and two atoms of sodium react with the cellulose to form the compound $C_6H_8O_3(ONa)O.CS.SNa$, thus confirming Cross and Bevan. In "ripening" there is at first a progressive decrease in viscosity, owing to the depolymerizing action of the excess of alkali, then an increase in viscosity as coagulation sets in. The stability is increased by the presence of a certain amount of free caustic soda; 100 cubic centimeters of a viscose solution containing 2 grams of cellulose and 6 to 9 grams of free caustic soda remained unchanged for 3 months. A larger amount of alkali decreased the stability. A sample of viscose after standing 5 days, and examined just prior to coagulation, had the composition $C_{24}H_{38}O_{18}(ONa)O.CS.SNa$.

According to Vieweg,[2] the mercerization of cellulose causes several cellulose units to combine. Immersion of cellulose in 18 per cent sodium hydroxide gives the compound $(C_6H_{10}O_5)_2.NaOH$. If the cellulose is pressed until it retains twice its weight of the alkaline solution, the compound $(C_6H_{10}O_5)_3.NaOH$ remains. The latter will combine with only 16 per cent of carbon bisulphide, based on the cellulose, so that the formula must be $(C_6H_{10}O_5)_3.CS_2.NaOH$. Titration with iodine showed that only the complexes $(C_6H_{10}O_5)_3$ and $(C_6H_{10}O_5)_4$, especially the latter, exist in solutions capable of spinning.

If ripening yields the $C_{24}:CS_2$ aggregate, then acid hydrolysis should yield more hydrogen suphide and less carbon bisulphide as ripening proceeds. Leuchs[3] found that this was not the case. Viscose ripened at periods varying from 2 to 6 days showed the ratio $CS_2:C_6H_{10}O_5$ to remain constant at 1:2. Hence the ripening process is considered to be colloidal rather than chemical. His methods are open to question.

Subjection of cellulose acetate to the viscose reaction gives a xanthate of the composition $C_6H_5(ONa)_3.(O.CS.SNa)_2$. In contrast with cellulose xanthate, it accordingly appears to contain five active hydroxyl groups.[4]

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[1] H. Ost, F. Westhoff, and L. Gessner, *Ann.*, **382** (1911), 349; *cf.* G. Bonwitt, *Z. angew. chem.*, **26** (1913), 89.

[2] W. Vieweg, *Zellstoff u. Papier*, **2** (1922), 18.

[3] K. Leuchs, *Chem. Ztg.*, **47** (1923), 801.

[4] R. Wolffenstein and E. Oeser, *Ber.*, **56** (1923), 785.

The inventors of the viscose process had in view the use of the viscous solution for coating fibers and fabrics. It remained for Stearn[1] to recognize that the progressive changes taking place in the ripening of viscose resulted in a product suitable for spinning filaments[2] and making films.

Considerable latitude is shown in the commercial methods for preparing viscose.[3] According to the methods of preparation, solutions having a wide range of properties can be obtained.

Laboratory Preparation of Viscose.—Immerse 37 grams of surgical cotton in 558 cubic centimeters of 17.5 per cent sodium hydroxide (sp. gr. 1.2) at 20° for 1.5 hours in a tightly stoppered bottle. Drain and press the cotton to a weight of 160 grams, pick it apart with forks, and preserve in a tightly stoppered bottle at 18° for 96 hours. To the alkali-cellulose in a closed rotating vessel, add 30 cubic centimeters of carbon bisulphide over a period of 2 hours. The color should be a deep orange yellow. Dissolve the cellulose xanthate by the gradual addition of 120 cubic centimeters of 4 per cent sodium hydroxide and 25 cubic centimeters of 10 per cent sodium suphite, using mechanical stirring. Add further amounts of 4 per cent sodium hydroxide if necessary until the viscosity by the falling-sphere method shows a reading of 20 millimeters in 30 seconds. Filter the solution through light filter cloth at a pressure of 40 pounds to the square inch; then subject it to a vacuum of 20 millimeters for 4 hours to remove air bubbles. Store the solution so obtained in a tightly stoppered bottle at 18° for 90 to 150 hours to age. To prepare a film, the solution is spread uniformly on a glass plate and exposed for 2 minutes to a coagulant consisting of: glucose, 10 per cent; sulphuric acid, 10 per cent; zinc sulphate, 1 per cent; anhydrous sodium sulphate, 14 per cent; and water, 65 per cent. The sheet is then washed, bleached with potassium permanganate followed by sulphurous acid, washed, and dried under tension.[1]

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[1] C. Stearn, *J. Soc. Dyers Colourists*, **19** (1903), 230; E. P. 1020, 1021, 1022 (1898); 7023 (1903); U. S. P. 716778 (1902).

[2] The world's production of artificial silk, now called rayon, reached 50,000 tons in 1923. Most of it is produced by the viscose process. In comparison with other artificial silks, viscose has the great advantage that the various manufacturing steps can be carried out entirely in aqueous solutions of cheap chemicals.

[3] F. J. G. Beltzer, *Kunsistoffe*, **2** (1912), 45; F. Becker, "Die Kuntseide" (1912), p. 270; B. M. Margosches, "Die Viskose" (1906).

Sulphite pulp is used almost entirely in the commercial preparation of viscose. Bleached pulp is usually employed, since to produce a satisfactory spinning solution and final product, the pulp should be free from lignin and coloring matter.[2] During conversion, "pure" bleached wood pulp will lose as much as 20 per cent of its weight, the largest loss being in the mercerization.[3] Purified cotton cellulose, on the other hand, shows a slight increase in weight on regeneration.[4]

According to Beltzer,[5] the wood pulp is purified by heating in a tank of pitch pine with hydrofluoric acid of 0.5 to 1.0° Bé. for 2 to 3 hours at 80°. This removes the silica and other inorganic compounds, and renders the organic impurities more easily soluble in alkali. After draining and washing, the pulp is boiled in sodium hydroxide of 1 to 2° Bé. for 3 to 4 hours, and again washed.

Previous to the preparation of the alkali-cellulose, the cellulose should be in a state of fine subdivision. It is also essential to mill or knead the mixture of cellulose and alkali thoroughly to obtain a uniform reaction.

A viscose solution of the highest viscosity is obtained by adding carbon bisulphide to the cellulose immediately after or during mercerization, if the temperature is kept low. According to the treatment given the alkali-cellulose or the viscose solution, solutions can be prepared having 5 and 20 per cent of cellulose and yet having the same viscosity.[6] Reduction in viscosity is obtained by storing the alkali-cellulose for a prolonged period or by heating it previous to the addition of the carbon bisulphide. The same end is also attained by a slight oxidation of the alkali-cellulose with sodium peroxide, or air in the presence of catalysts.[7] As previously mentioned, reduction in viscosity is produced by keeping the viscose solution at room temperature for several days. Ripening is hastened by heating, this result being secured by heating at 50 to 60° for 2 hours or for a shorter time at temperatures up to 90°.

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[1] F. D. Snell, *J. Ind. Eng. Chem.*, **17** (1925), 198; *cf.* E. H. Morse, *Ibid.*, **18** (1926), 398–400.

[2] L. P. Wilson, *J. Soc. Chem. Ind.*, **39** (1920), 266R.

[3] C. Beadle, *J. Franklin Inst.*, **143** (1897), 3.

[4] C. F. Cross and E. J. Bevan, "Cellulose" (1916), p. 28.

[5] F. J. G. Beltzer, *Kunststoffe*, **2** (1912), 42.

[6] C. Beadle, *J. Franklin Inst.*, **138** (1894), 103.

[7] L. P. Wilson, *J. Soc. Chem. Ind.*, **39** (1920), 177T.

The use of hydrocellulose permits obtaining a viscose solution of lower viscosity and with a smaller consumption of chemicals. Wood pulp that has been heated with dilute mineral acids can be converted into viscose with only 30 to 40 per cent of the quantities of sodium hydroxide and carbon bisulphide usually employed.[1]

Viscose solutions on standing coagulate spontaneously, forming a solid mass in the containing vessel. Shrinkage then sets in, a tough mass of gelatinized cellulose surrounded by a yellow alkaline solution being finally obtained. The coagulated viscose, if dilute, contracts to 10 per cent of cellulose and 90 per cent of water. If stronger than 10 per cent it will take up water and expand.[2] The coagulum is not dehydrated by treatment with alcohol.

The stability of viscose solutions is greatly increased by low temperatures. They are usually stored at temperatures 1 to 2° above zero. Coagulation requires about 14 days at 10° and under, and 6 to 10 days at 10 to 20°.[3] According to Beadle,[4] a solution that would keep 40 days at 1.7°, would coagulate in 25 days at 8.3°, or in 6 days at 18.3°. A thin film on glass will coagulate in a few minutes at a temperature of 121.° Small amounts of viscose coagulate more rapidly than large amounts at a given temperature. Coagulation is also influenced by the amount of free alkali present in the solution.

Addition of strong mineral acids decomposes the viscose and causes immediate coagulation. Acetic acid, on the other hand, will neutralize the free alkali, but will not decompose the viscose. Alcohol and solutions of salts, such as sodium chloride, precipitate sodium cellulose-xanthogenate that can be redissolved in water. These properties can be used in the purification of viscose. For example, the free alkali can be neutralized with acetic acid and the viscose precipitated with alcohol. On washing the precipitate with alcohol most of the sodium acetate and other impurities are removed. Resolution in water is greatly aided by the presence of sodium hydroxide.

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[1] W. Cross, E. P. 185433 (1921); *cf.* C. F. Cross, G. P. 92590 (1896).

[2] C. Beadle, *l.c.*, 105.

[3] C. F. Cross, cited by B. M. Margosches, "Die Viskose," p. 70.

[4] C. Beadle, *l.c.*, 104.

The magnesium, sodium, and potassium salts of cellulose xanthogenate are soluble in water. The metal salts are insoluble and exhibit a variety of colors, the latter varying with the purity of the viscose solution.

The suitability of a viscose for the preparation of artificial silk may be determined by forcing a fine stream of the solution into 40 per cent acetic acid. If properly matured, coagulation takes place at once; otherwise the viscose passes into solution. Besides the sodium cellulose-xanthogenate, sulphides, polysulphides, and thiocarbonates are present as impurities. It has not been found expedient, however, to purify the solution before spinning.[1] The viscose solution is forced by high pressure through fine orifices into a coagulating bath. Sulphuric acid and sodium acid sulphate are usually used as coagulants on account of their cheapness, in which case gelatinized cellulose is obtained at once. A modification consists in forming a thread of coagulated sodium cellulose-xanthogenate by means of salts, followed by a second bath to convert it to cellulose.

The artificial silks, particularly viscose, have the disadvantage of greatly reduced strength in the wet state. To overcome this defect, the fiber is treated with formaldehyde in the presence of sodium hydroxide[2] or acids,[3] a condensation taking place between the aldehyde and the cellulose. This is known as the "sthenosage"[4] or strengthening process. The sthenosized fiber is harder, and in the dry state shows a slight increase in tensile strength, but decreased elasticity. In the wet state, in comparison with the untreated fiber, the tensile strength is two to three times greater. The difficulty in stopping the reaction at the point of optimum strength and elasticity has apparently prevented the operation of the process on an industrial scale.[5]

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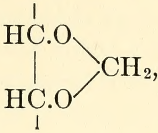
[1] V. Hottenroth, "Ullmann Enzykl. Techn. Chem.," **7** (1919), 335.

[2] E. R. Blumer G. P. 179590 (1906).

[3] X. Eschalier, F. P. 374724 (1906).

[4] Σθενος, strength.

[5] V. Hottenroth, *l.c.*, 323.

Sthenosized fibers cannot be mercerized or made to undergo the viscose reaction.[1] They are not stained blue by iodine-potassium iodide solution and are only feebly colored by direct cotton dyes. A true formal derivative,  $\begin{matrix} | \\ HC.O \\ | \\ HC.O \\ | \end{matrix}\!\!>CH_2$, appears to be formed, since the whole of the combined formaldehyde can be recovered by heating with dilute sulphuric acid. According to Samec,[2] the formaldehyde first reacts with a hydroxyl group to form the group $-\overset{|}{\underset{|}{C}}.OCH_2OH$ that, in turn, reacts with an adjacent hydroxyl group to form an inner anhydride. The fixation of formaldehyde appears to increase with the degree of gelatinization, though large quantities are taken up by hydrocellulose and oxycellulose.

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[1] F. J. G. Beltzer, *Eighth Int. Cong. Appl. Chem.*, N. Y., **7** (1912), 9.

[2] M. Samec and S. Ferjancic, *Kolloidchem. Beihefte*, **14** (1921), 209.

CHAPTER VIII

OXYCELLULOSE

The recognition of oxycellulose as a distinct modification of cellulose is due to Witz.[1] While examining cotton fabrics that had been accidentally overbleached, he noticed that the edges of the resulting holes had a marked affinity for basic dyes, particularly methylene blue. The characteristic product could be obtained by the use of oxidizing agents, such as chlorine, potassium permanganate, hydrogen peroxide, and chloric and chromic acids. Analysis showed it to contain less carbon and more oxygen than normal cellulose—hence it was given the name *oxycellulose.*[2]

Formation with Nitric Acid.—Cellulose when boiled with 60 per cent nitric acid gave, in addition to oxalic acid, about 30 per cent of oxycellulose.[3] On removing the acid with hot water, the mass became gelatinous and resembled horn after drying. It was entirely soluble in dilute alkali and could be precipitated unchanged by acids, alcohol, salt solutions, and even by strong solutions of the caustic alkalis. As a result of a difference in properties, Cross and Bevan[4] called their product, obtained with nitric acid, β-oxycellulose, and that of Witz with bleaching powder, α-oxycellulose.

The gelatinous product obtained by Sacc[5] by boiling spruce wood with nitric acid was believed to be pectic acid. Lindsey and Tollens,[6] who repeated Sacc's work, obtained a gelatinous oxycellulose completely soluble in dilute ammonia and in very dilute caustic soda; strong caustic soda precipitated it as a jelly.

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[1] G. Witz, *Bull. Rouen,* **10** (1882), 416–464; **11** (1883), 169–232.

[2] G. Witz, *l.c.,* 448.

[3] C. F. Cross and E. J. Bevan, *J. Chem. Soc.,* **43** (1883), 22–23.

[4] C. F. Cross and E. J. Bevan, *J. Soc. Chem. Ind.,* **3** (1884), 206.

[5] F. Sacc, *Ann. chim. phys.,* [3] **25** (1848), 218.

[6] J. B. Lindsey and B. Tollens, *Ann.,* **267** (1892), 366–370.

Using the procedure of Cross and Bevan, von Faber and Tollens[1] obtained a yield of 70 per cent of oxycellulose from cotton. Nastjukoff[2] obtained a yield of 90 per cent of β-oxycellulose, completely soluble in hot ammonium hydroxide, by heating 1 part of cellulose with 2.5 parts of nitric acid (sp. gr. 1.3) on the water bath for 1 hour. Bull[3] prepared this product by heating 75 grams of cotton and 750 grams of 60 per cent nitric acid in a stoppered retort on a water bath for 24 hours and returning the distillate at intervals. After filtering, washing with nitric acid, 60 per cent alcohol, 90 per cent alcohol, and finally with ether, the yield was 35 per cent. The oxycellulose dissolved completely in water and gave opalescent solutions with aqueous solutions of ammonia, pyridine, piperidine, sodium carbonate, and weak solutions of sodium and potassium hydroxides. Excess of sodium hydroxide produced gelatinization, while a large excess produced a clear and limpid mass. Acids precipitated it in a gelatinous state. The substance which was regenerated from the nitrate of the oxycellulose with ammonium sulphide was apparently not β-oxycellulose, since it no longer swelled in water and dissolved to only a slight extent in dilute sodium hydroxide. This behavior is difficult to explain unless the original oxycellulose consisted largely of a material related to Guignet's soluble cellulose[4] and was rendered insoluble by the strong nitrating acids.

The oxycellulose when freshly prepared with nitric acid is not colored by iodine or by Schultze's reagent (zinc chloride and iodine-potassium iodide), but the horny mass to which it dries is colored deep blue by the latter.[5] According to others, the fresh material is also colored bluish violet.[6] Iodine and sulphuric acid color oxycellulose (by chloric acid) more rapidly and distinctly than it does cellulose.[7]

Oxycellulose by Chloric Acid.—When paper has been written upon with chloric acid or aluminum chlorate, dried at 50 to 60°, washed, and then dyed with methylene blue, the writing is colored a dark purplish blue.[1]

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[1] O. von Faber and B. Tollens, *Ber.*, **32** (1899), 2594.

[2] A. Nastjukoff, *Ber.*, **34** (1901), 3589.

[3] B. S. Bull, *J. Chem. Soc.*, **71** (1897), 1090–1097.

[4] C. E. Guignet, *Compt. rend.*, **108** (1889), 1258.

[5] C. F. Cross and E. J. Bevan, *J. Chem. Soc.*, **43** (1883), 23.

[6] B. S. Bull, *l.c.*; J. B. Lindsey and B. Tollens, *l.c.*, 368.

[7] L. Vignon, *Compt. rend.*, **125** (1897), 449.

Vignon[2] considered the best method of preparing oxycellulose to be as follows: 30 grams of purified cotton are placed in a boiling solution of 150 grams of potassium chlorate in 3 liters of water, and 125 cubic centimeters of 35 per cent hydrochloric acid are gradually added. After maintaining at the boiling point for an hour, the oxycellulose is washed with water by decantation until free from acid, then with alcohol, and air dried. The yield is 96 per cent.[3]

On treating oxycellulose prepared as above with a 28 per cent solution of potassium hydroxide and filtering, there was obtained a residue, amounting to 60 per cent, having the properties of cellulose.[4] Slow addition of the filtrate to a cooled solution of hydrochloric acid caused separation of 10 per cent of a white substance called "soluble cellulose." Except for its solubility in alkali, it is not apparent why the product should have been so named, since its solubility in 1 liter of cold and of boiling water was only 0.02 and 0.4 gram, respectively. Ultimate analysis showed it to have the composition of cellulose, but it differed therefrom in its heat of formation and other properties. It contained 3.5 per cent moisture, gave about 5.0 per cent furfural on distillation with hydrochloric acid, reduced Fehling's solution, and gave a rose color with Schiff's reagent. It was soluble in the caustic alkalis, partially in hydrochloric acid, and completely so in nitric acid. The product probably consists of a mixture of oxycellulose, hydrocellulose, and colloidal cellulose.

Oxycellulose by Chromic Acid.—The oxycellulose is prepared as follows: 40 grams of cotton are placed in a solution of 60 grams of potassium bichromate and 80 grams of sulphuric acid in 3 liters of water, and boiled for 1 hour. There is obtained 69 per cent of a green powder with 2.24 per cent ash.[5] A similar high retention of chromium oxide was observed by Cross and Bevan.[1] Heuser[2] obtained a yield of 83 per cent of oxycellulose having 0.56 per cent ash after washing with hot 2 per cent sulphuric acid.

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[1] H. Schmid, *Wagner's Jahresber.*, **29** (1883), 1076–1078; *cf.* G. Witz, *Bull. Rouen*, **11** (1883), 201.

[2] L. Vignon, *Compt. rend.*, **125** (1897), 449.

[3] E. Heuser and F. Stöckigt, *Cellulosechemie*, **3** (1922), 66.

[4] L. Vignon, *Compt. rend.*, **136** (1903), 969–970.

[5] L. Vignon, *Bull. soc. chim.*, **19** (1898), 811; *cf.* G. Witz, *Bull. Rouen*, **11** (1883), 207.

Oxycellulose by Permanganates.—The oxidizing action on cellulose of potassium permanganate alone, and with the addition of acids and alkalis, has been studied by various investigators.[3] As pointed out by Witz, oxidation in alkaline solution tends to the formation of completely soluble products rather than oxycellulose.[4]

An oxycellulose having high reducing properties is prepared as follows:[5] 30 grams of filter paper are treated with 600 to 900 cubic centimeters of 6.5 per cent sodium hydroxide solution and shaken until a pulp is formed. The pulp is then thinned with water, rendered acid with sulphuric acid, filtered off by suction, and washed with water. The moist pulp is suspended in 600 to 900 cubic centimeters of 7.5 per cent sulphuric acid and rapidly stirred mechanically. By means of a separatory funnel, 12 grams of potassium permanganate that has been dissolved in 7.5 per cent sulphuric acid are slowly added. If 1 to 2 hours are taken for the addition, the solution is completely decolorized in 4 hours from the start. The finely divided brown precipitate is filtered off, suspended in dilute suphuric acid, and decolorized with hydrogen peroxide. It is then washed with water until free from acid and manganese sulphate, and dried at a temperature not exceeding 40° to prevent the formation of a horny mass. The yield is 94.5 per cent.

The oxycellulose on heating with sodium hydroxide solution (8 to 10 per cent) on the water bath for 5 hours gives a golden-yellow solution changing to brown. Probably as a result of oxidation, only a slight precipitate is obtained on acidification. It dissolves to a deep-yellow solution in 5*N* sodium hydroxide;

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[1] C. F. Cross and E. J. Bevan, *Chem. News*, **64** (1891), 63.

[2] E. Heuser and F. Stöckigt, *Cellulosechemie*, **3** (1922), 66.

[3] G. Witz, *Bull. Rouen*, **11** (1883), 211; A. Nastjukoff, *Ber.*, **33** (1900), 2237; **34** (1901), 720; J. Allan, *J. Soc. Dyers Colourists*, **14** (1898), 6; H. Moore, *Ibid.*, **31** (1915), 180.

[4] J. Allan, *J. Soc. Dyers Colourists*, **14** (1898), 6.

[5] E. Knecht and L. Thompson, *J. Soc. Dyers Colourists*, **36** (1920), 251; *cf.* E. Heuser and F. Stöckigt, *Cellulosechemie*, **3** (1922), 66.

this on neutralization gives an acid cellulose of only slight reducing power.

Knecht's oxycellulose has a copper number of 14.2 compared with 7.6 for Nastjukoff's oxycellulose prepared with bleaching powder. It has strong aldehydic properties but is only slightly acidic. It reduces solutions of silver, cupric and ferric salts, and, especially in the presence of alkalis, such dyes as indigo, methylene blue, safranine, and rosinduline.

On following, by means of the copper numbers, the action on cotton of gradually increased amounts of potassium permanganate in 7.5 per cent sulphuric acid, it was found that initially the reducing value was proportional to the oxygen consumed. With one-half atom of oxygen the copper number was 12.7, while with one atom of oxygen this value increased to only 14.0, indicating that while aldehydic and ketonic groups are formed for the most part, further oxidation then takes place to the carbonyl group.[1]

Oxycellulose by Hypochlorites.—Nastjukoff[2] used solutions of bleaching powder of 4 and 12° Bé. With the stronger solution the oxidized cellulose was almost completely soluble in a 10 per cent solution of sodium hydroxide.

The oxycellulose prepared by Qvist[3] from sulphite pulp with sodium hypochlorite had the following properties:

Copper number (uncorrected)	34.6
Solubility in 10 per cent NaOH	81.7 per cent
Moisture	9.52 per cent

In the case of hypochlorites, moderate additions of acid decrease the amount of oxycellulose formed, while with alkali a minimum amount of oxycellulose is formed at a concentration of 1 gram of sodium hydroxide to a liter of sodium hypochlorite containing 11.47 grams of chlorine.[4] The conversion of cellulose to oxycellulose by hypochlorites is promoted greatly by the presence of oxides of mercury, copper, cobalt, nickel, iron, and chromium.[5]

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[1] E. Knecht, *J. Soc. Dyers Colourists*, **38** (1922), 132–136.

[2] A. Nastjukoff, *Ber.*, **33** (1900), 2237.

[3] W. Qvist, *Papier-Fabr.*, **17** (1919), 821.

[4] H. Moore, *J. Soc. Dyers Colourists*, **31** (1915), 180.

[5] P. Weyrich, *Z. angew. Chem.*, **28** (1915), Ref. 399; W. Thomson, *J. Soc. Dyers Colourists*, **30** (1914), 142.

Oxycellulose has also been prepared by the action of bromine in the presence of calcium carbonate.[1] Dry bromine is without action on dry cellulose.[2] This is true also of the other halogens. According to Klemm,[3] iodine is without chemical action on cellulose in either a wet or a dry condition. Cotton and wood pulps absorb appreciable quantities of iodine; if, after standing some hours, sodium hydroxide is added and the mixture steam distilled, appreciable quantities of iodoform are obtained.[4] The residual cellulose on retreatment continues to form iodoform. Wood cellulose gives more iodoform than cotton; 10 grams of poplar pulp gave 0.15 gram of iodoform. Collie[5] obtained carbon tetrabromide by treating cellulose with a hypobromite and distilling.

Oxycellulose by Salts and Air.—It has been stated that oxycellulose is produced by heating moist cotton at 50° with salts of copper, cobalt, manganese, nickel, iron, and chromium, their activity being in the order mentioned.[6] Certain salts also form hydrocellulose under the same conditions.

Paper coated with ink rich in iron oxide, or when coated with colloidal ferric oxide, is converted into a powder having a microcrystalline structure by heating in a current of dry air at 50 to 60° for 5 to 6 hours.[7] According to Bolton and Dorée,[8] no tendering takes place with colloidal ferric oxide prepared from ferric chloride when it is free from hydrochloric acid. In the presence of the acid, hydrocellulose is formed. It is a common observation, however, that when a cotton string is attached to iron and left in a moist atmosphere, the string in time becomes impregnated with rust and loses strength at the point of attachment.

Calico mordanted with chromium, and then treated with warm hydrogen peroxide in the presence of ammonia or sodium hydroxide, gradually disintegrates, with the formation of oxycellulose. In the absence of chromium, there is no material change.[1]

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[1] O. von Faber and B. Tollens, *Ber.*, **32** (1899), 2589.

[2] A. P. N. Franchimont, *Rec. trav. chim.*, **2** (1883), 91.

[3] P. Klemm, *Wochbl. Papierfabr.*, **43** (1912), 464.

[4] J. Huebner and J. N. Sinha, *J. Soc. Chem. Ind.*, **42** (1923), 255–260T.

[5] J. N. Collie, *J. Chem. Soc.*, **65** (1894), 262–264.

[6] L. L. Lloyd, *J. Soc. Dyers Colourists*, **26** (1910), 273.

[7] K. Haertling, *Kolloid Z.*, **25** (1919), 74–79.

[8] H. S. Bolton and C. Dorée, *J. Soc. Dyers Colourists*, **40** (1924), 292.

A salt such as mercuric chloride is reduced by cellulose, apparently with the formation of oxycellulose.[2]

Oxycellulose by Alkalis and Air.—Blondel[3] observed that the hydroxides and carbonates of the alkalis in the presence of air caused a weakening of cotton and produced a greater affinity for dyes, with the exception of the azo colors.

Cotton in the presence of alkali and air may be severely oxidized. The following table shows the losses suffered by cotton that had been scoured, bleached, and dried at 85°:

5 per cent of	Loss in per cent with			
	Oxygen	Steam and oxygen	Air	Steam and air
$NaOH$	11.05	17.3	5.2	9.2
KOH	22.8	29.8	8.4	11.7
Na_2CO_3	8.2	10.1	3.9	5.4
K_2CO_3	13.7	16.4	5.3	6.9
$Na_2B_4O_7$	5.9	6.8	2.2	2.8
Na_2HPO_4	3.1	3.5	2.05	2.3

The residual fiber was weak, owing to the presence of oxycellulose.[4] Thies[5] found a very decided formation of oxycellulose when cotton was treated with concentrated alkalis saturated with oxygen. The fiber decreased about 80 per cent in strength.

Oxycellulose by Hydrogen Peroxide.—The formation of oxycellulose with hydrogen peroxide was first studied by Witz.[6] The action on cotton is greatly increased in the presence of the oxides of iron, chromium, aluminum, and magnesium, those of iron and chromium being particularly effective.[1] The alteration of the cellulose is much greater if the cotton has been mercerized previous to treatment with hydrogen peroxide. The fiber disintegrates completely if sufficient sodium hydroxide is added to the oxidizing solution to bring it to 5 to 6° Bé.

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[1] E. Knecht, *J. Soc. Dyers Colourists*, **13** (1897), 109.

[2] L. Vignon, *Compt. rend.*, **116** (1893), 517, 645.

[3] E. Blondel, *Bull. Rouen*, **10** (1882), 472.

[4] C. O. Weber, *J. Soc. Chem. Ind.*, **12** (1893), 118–119; *cf.* S. R. Trotman and S. J. Pentecost, *Ibid.*, **29** (1910), 4.

[5] F. H. Thies, *Färber-Ztg.*, **24** (1913), 393.

[6] G. Witz, *Bull. Rouen*, **11** (1883), 197.

By the action of two parts of 50 per cent hydrogen peroxide on cellulose for 2 months, Bumcke and Wolffenstein[2] obtained a product that they named "hydralcellulose." It reduced Fehling's solution and ammoniacal silver solution, colored Schiff's reagent, and formed hydrazones containing 1.71 per cent of nitrogen, thereby showing its aldehydic properties. On treatment with alkali, the aldehyde presumably followed the Cannizarro reaction, being converted into an insoluble alcohol, cellulose, and a soluble acid, acid cellulose, the latter having no aldehydic properties. There was formed one part of acid cellulose to two parts of cellulose.

Acid cellulose dissolves in concentrated hydrochloric acid, from which it can be precipitated unchanged by water. On heating the solution or allowing it to stand, hydrolysis takes place very readily. Drying produces loss of solubility, especially in sodium hydroxide, and formation of a hard, brittle mass having the lactone formula, $C_{36}H_{60}O_{31}$. Acid cellulose may also be formed by boiling cellulose with a 30 per cent sodium hydroxide solution for an hour.

Acid cellulose is sufficiently acid to decolorize phenolphthalein. Cellulose, hydralcellulose, and acid cellulose lactone from Schweizer's reagent and from boiling sodium hydroxide solution were nitrated by heating with four parts of nitric acid (86 per cent) at 85°. Practically identical products were obtained when examined as to: nitrogen content (8 per cent) of the portions soluble in alcohol and acetone; explosion point; and optical rotation. The molecular weight of the alcohol-soluble portion of the nitrated celluloses, determined in boiling acetone, gave an average molecular weight of 1350, so that hydralcellulose has the formula $6C_6H_{10}O_5 + H_2O$.

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[1] M. PRUD'HOMME, *Bull. Mulhouse*, **61** (1891), 508; *Compt. rend.*, **112** (1891), 1374.

[2] G. BUMCKE and R. WOLFFENSTEIN, *Ber.*, **32** (1899), 2493–2507; *cf. Ibid.*, **34** (1901), 2415–2417.

The assumption of the hydrolysis of cellulose to aldehydic hydralcellulose by hydrogen peroxide is based on the work of Wurster,[1] who states that cane sugar is first inverted by hydrogen peroxide, then oxidized with evolution of carbon dioxide. Cellulose is scarcely attacked by hydrogen peroxide at low temperatures, but rapidly at the boiling point in alkaline or acid solution, with the formation of glucose and dextrin. According to Haller,[2] vegetable fibers are dissolved by the prolonged action of hydrogen peroxide, with the formation of dextrose, cellulose peroxide being an intermediate product. Chromium oxide hastens the decomposition, while aluminum oxide retards it.

Haeussermann[3] claims that the acid cellulose of Bumcke and Wolffenstein does not contain a carboxyl group, while Bay[4] believes it to be a mixture of hydrated cellulose and oxycellulose. In view of our present knowledge of hydralcellulose it should be classed as an oxycellulose.

Oxycellulose prepared with hydrogen peroxide sometimes has an irritating action on the skin.[5]

Oxycellulose from Cuprammonium Solution.—Cuprammonium solution behaves towards cotton like hydrogen peroxide. Even though the solution is not sufficiently strong to dissolve the cellulose, the latter is oxidized and colored strongly by methylene blue.[6] According to Bumcke and Wolffenstein,[7] the cellulose precipitated from Schweizer's reagent is an acid cellulose.

Oxycellulose by Reduction of Cellulose Nitrate.—According to Vignon,[8] the product of the reduction of the cellulose nitrates with ferrous chloride is oxycellulose and not cellulose. Reduction with ammonium sulphide gives a product devoid of reducing properties. It is possible that in this case the reducing bodies are dissolved by the alkaline ammonium sulphide. Various products showed the following reduction with Pasteur's solution:

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[1] C. Wurster, *Ber.*, **22** (1889), Ref. 145.

[2] R. Haller, *Chem. Zentr.*, **91,** IV (1920), 543.

[3] C. Haeussermann, *Z. Schiess-u. Sprengstoff*, **1** (1906), 39, 305.

[4] C. Bay, Diss. Giessen (1913).

[5] C. G. Schwalbe and E. Becker, *Zellstoff u. Papier*, **1** (1921), 102.

[6] M. Prud'homme, *Compt. rend.*, **112** (1891), 1374.

[7] *L.c.*

[8] L. Vignon, *Compt. rend.*, **131** (1900), 530.

	Grams CuO per 100 Grams Substance
Oxycellulose	10.36
Cellulose nitrate	13.71
Oxycellulose reduced by $FeCl_2$	10.42
Cellulose nitrate reduced by $FeCl_2$	11.70
Oxycellulose nitrate reduced by $FeCl_2$	10.83

Cellulose nitrate is a derivative of oxycellulose.[1] Dried at 80° it had the following composition:

	Per Cent
C	23.89
H	2.44
N	13.94
O	59.73

These results agree with the formula:

$$3[C_6H_7(NO_2)_3O_5] + C_6H_7(NO_2)_3O_6 = C_{24}H_{28}(NO_2)_{12}O_{21}.$$

Berl and Fodor[2] likewise believe that cellulose nitrate is a derivative of oxycellulose. Obviously, little reliance can be placed on ultimate analysis in detecting the presence of an extra atom of oxygen in so large a molecule.

Oxycellulose by Electrolysis.—Cellulose in contact with the anode is converted into oxycellulose during the electrolysis of aqueous solutions.[3]

When a neutral 15 per cent solution of potassium chloride containing cellulose is electrolyzed, the cellulose is ultimately converted into soluble products. If the reaction is stopped after 60 to 70 per cent of the cellulose has disappeared, the residue dissolves completely in 10 per cent sodium hydroxide. On prolonging the treatment, the oxycellulose forms a stable colloidal solution in water. The oxycellulose showed a low viscosity by Ost's method[4] and copper numbers as high as 39.5. Hydrolysis with 72 per cent sulphuric acid gave 90 per cent of glucose. The high "hydrolysis difference" number, and other properties indicated that the product was a hydro-oxycellulose.[1] Cellulose is also converted into hydro-oxycellulose by treatment with chlorine and the hydrochloric acid resulting therefrom.[2] It is apparent that this product may be formed by any acid oxidizing agent.

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[1] L. Vignon, *Compt. rend.*, **131** (1900), 509; **136** (1903), 898.

[2] E. Berl and A. Fodor, *Z. Schiess-u. Sprengstoff*, **5** (1910), 254, 269.

[3] G. Gopplsroeder, *Bull. Mulhouse*, **45** (1875), 229; J. J. Hummel, *J. Soc. Chem. Ind.*, **4** (1885), 306; G. Witz, *Bull. Rouen*, **11** (1883), 196.

[4] H. Ost, *Z. angew. Chem.*, **24** (1911), 182.

Cellulose Peroxide.—In 1906, attention was called by Cross and Bevan[3] to the fact that cellulose which had been bleached without the subsequent use of an antichlor apparently formed a cellulose peroxide. The active oxygen was retained for a long time. Iodine was liberated from potassium iodide solution and this property was not destroyed by washing with water or by neutralizing the acidity of the product. Boiling water or an antichlor destroyed its activity. The active oxygen disappeared on heating at 100°, leaving the fiber in the form of oxycellulose. The peroxide reaction does not always disappear on drying, and apparently does not result in a decrease of the strength of linen yarn.[4]

The phenomenon is characteristic of bleached pulps, and is apparently not due to the presence of residual chlorine or hypochlorite,[5] as suggested by Zimmermann.[6]

A cellulose peroxide is also produced by the careful heating of cellulose in an acid solution of a persulphate, particularly ammonium persulphate, and allowing to cool. The compound decomposes at 100° with the formation of oxygen, carbon dioxide, and a very irritating gas.[7] The amount of active oxygen fixed is only 0.015 per cent. When suspended in water and methyl orange added, the ordinary yellow color results; but on the addition of a neutral salt, such as sodium chloride, the liquid turns red. This shows the acid character of the product and the presence of oxycellulose.[8]

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[1] R. Oertel, *Z. angew. Chem.*, **26** (1913), 246–250; *Chem. Ztg.*, **35** (1911), 713.

[2] C. C. Budde, E. P. 184610 (1921).

[3] C. F. Cross and E. J. Bevan, *Z. angew. Chem.*, **19** (1906), 2101–2102; *Papier-Ztg.*, **32** (1907), 87–88.

[4] J. L. Heinke, *Chem. Ztg.*, **31** (1907), 974.

[5] K. Rieth, *Wochbl. Papierfabr.*, **38** (1907), 394; Montanus, *Ibid.*, 1041.

[6] D. M. R. Zimmermann, *Z. angew. Chem.*, **20** (1907), 1280.

[7] H. Ditz, *Chem. Ztg.*, **31** (1907), 833–834, 857–885.

[8] H. Ditz, *Chem. Ztg.*, **31** (1907), 844–845.

Cotton treated with a solution of 20 grams of ammonium persulphate per liter, dried, and steamed for 134 hours decreased in strength 41 per cent.[1]

Kolb[2] observed that linen exposed to the action of ozone for a week was attacked; and Witz[3], by means of methylene blue, detected the presence of oxycellulose. Moist filter paper exposed to a stream of ozone of a concentration of 2 per cent showed no rise in temperature.[4]

Ozone in concentrations of 1 to 2 per cent rapidly attacks cotton with the formation of cellulose peroxide, an acid derivative, and some carbon dioxide.[5] The ozonized fiber rapidly reduces Fehling's solution but not ammoniacal silver solution. In the absence of water only a small amount of peroxide is formed, but much more in air-dried cotton.[6] The activity of cellulose peroxide soon disappears in air, but remains for some weeks in the product kept in a dry atmosphere. It is slowly decomposed by water, with the formation of hydrogen peroxide. It is decomposed to the extent of 25 per cent on heating for 2 hours at 37°, and almost completely after 2 hours at 95°. After 18 hours' exposure to ozone, various forms of cellulose contained the following amounts of "active ozone":

	PER CENT
Cotton (air dry)	0.0056
Mercerized cotton	0.0106
Lustra-cellulose	0.0248

Cellulose peroxide, through liberation of hydrogen peroxide, acts strongly on photographic plates, negative images of the fibers being obtained after 6 hours' exposure at 37°.

Cotton and mercerized cotton, after continuous exposure for 24 hours to ozonized oxygen containing 1.5 to 2.0 per cent ozone, had the following properties:[7]

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[1] A. SCHEURER, *Bull. Mulhouse*, **71** (1901), 182.

[2] J. KOLB, *Bull. Mulhouse*, **38** (1868), 914.

[3] G. WITZ, *Bull. Rouen*, **11** (1883), 187.

[4] E. ERDMANN and H. STOLTZENBERG, *Chem. Zentr.*, **79** ,II (1908), 457.

[5] M. CUNNINGHAM and C. DORÉE, *J. Chem. Soc.*, **101** (1912), 497–512.

[6] C. DORÉE, *J. Chem. Soc.*, **103** (1913), 1347.

[7] C. DORÉE, *J. Soc. Dyers Colourists*, **29** (1913), 208.

	Cotton		Mercerized cotton	
	Normal	Ozonized	Normal	Ozonized
Loss in weight, per cent	....	12.0	....	7.0
Carbon, per cent	44.4	43.5	43.2	43.5
Methylene blue absorption, per cent	0.3	2.1	0.4	3.1
Copper number	1.2	16.9	1.7	24.0
Loss in 10 per cent KOH, per cent	....	64.0	....	57.0

Properties of Oxycellulose.—The property of cellulose peroxide of liberating iodine from a solution of potassium iodide is usually used for its detection.

The heats of combustion of oxycellulose in comparison with other carbohydrates are given below.[1] The heat of combustion of the residue from the treatment of the oxycellulose with potassium hydroxide agrees well with that for cellulose.

	CALORIES
Oxycellulose (by $KClO_3 + HCl$)	4124–4133
Oxycellulose exhausted by KOH of 30° Bé	4201
Portion precipitated by acid	3929
Cellulose	4190–4225
Sucrose	3955
Purified cotton (dried at 100°)	4223
Mercerized cellulose*	3980
Cellulose precipitated from Schweizer's reagent*	3982

* Dried in vacuo over H_2SO_4.

Oxycellulose has a marked affinity for basic dyes,[2] but only a very slight one for tetrazoic dyes. According to Harrison,[3] the dyeing properties of oxycellulose are due mainly to the colloidal state of the cellulose portion. This accounts for the fact that certain forms of hydrocellulose and mercerized cellulose dye with methylene blue in a manner similar to oxycellulose.

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[1] L. VIGNON, *Compt. rend.*, **125** (1897), 450; **127** (1898), 873; **131** (1900), 709.

[2] G. WITZ, *Bull. Rouen*, **10** (1882), 455; L. VIGNON, *Compt. rend.*, **125** (1897), 550; **131** (1900), 558.

[3] W. HARRISON, *J. Soc. Dyers Colourists*, **28** (1912), 360.

Oxycellulose has the power of adsorbing vanadium salts from solutions as dilute as one part per million, as can be shown by the subsequent effect of the fiber in developing aniline black.[1] It, however, shows no such intense adsorption for copper, aluminum, and iron mordants. The extent of adsorption increases in the order given.[2]

There appears to be no industrial use for oxycellulose. It has been suggested for calico printing[3] and as a binding or coating agent[4] for paper. An attempt to use an alkaline solution as a mordant for basic dyes gave negative results.[5] In paper making, the presence of a certain amount of oxycellulose facilitates gelatinization of the fibers by beating.

Effect of Heat.—The statement[6] that hydrocellulose becomes brown at 130 to 150°, at which temperature oxycellulose shows only a pale-yellow color, must be accepted with reservation. Pure hydrocellulose is stable at these temperatures and much more resistant to heat than oxycellulose.

When treated with alkaline salts, dried, and steamed, oxycellulose turns brown and becomes about 100 times darker than cellulose. Hydrocellulose is ultimately colored less than cellulose. The chief cause of the yellow coloration of cotton is attributed to the presence of β-oxycellulose.[7]

Esters of Oxycellulose.—The oxycellulose nitrate prepared by Cross and Bevan[8] corresponded with the compound $C_{18}H_{23}O_{16}(NO_3)_3$ and contained 6.48 per cent of nitrogen. Bull,[9] however, obtained an ester with 12.2 per cent of nitrogen from β-oxycellulose prepared with nitric acid. The nitrates of cellulose, hydrocellulose, and oxycellulose contain about the same amount of nitrogen.[10] Their stability in air and their resistance to alkalis decrease in the above order. All three nitrates reduce Fehling's solution, the nitrate of oxycellulose showing the greatest aldehydic property.

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[1] G. Witz and F. Osmund, *Bull. soc. chim.*, **45** (1886), 309–315.

[2] W. D. Bancroft, *J. Phys. Chem.*, **19** (1915), 167.

[3] C. Kurz, *Z. Farben-und Textilchem.*, **1** (1902), 46–47.

[4] E. Fues, G. P. 193909 (1906).

[5] J. Allan, *J. Soc. Dyers Colourists*, **14** (1898), 7.

[6] E. Justin-Mueller, *Bull. soc. chim.*, **29** (1921), 987–988.

[7] M. Freiberger, *Z. angew. Chem.*, **31** (1918), Ref. 146.

[8] C. F. Cross and E. J. Bevan, *J. Chem. Soc.*, **43** (1883), 22.

[9] B. S. Bull, *J. Chem. Soc.*, **71** (1897), 1096.

[10] L. Vignon, *Compt. rend.*, **126** (1898), 1658.

Knecht[1] found that oxycellulose (by $KMnO_4 + H_2SO_4$) acetylated more slowly than the original cellulose, but eventually reached about the same degree of esterification. On nitration, a distinct suppression of hydroxyl activity was noted, the oxycellulose nitrate containing only 11.5 per cent of nitrogen in comparison with 13.4 per cent for the nitrate prepared from the original cellulose.

Oxycellulose, after acetylation,[2] retained its aldehydic properties, and apparently contained four acetyl groups. It should not be assumed, however, that, as a result, there are three secondary alcohol groups in the oxycellulose.

Oxycelluloses on acetolysis by the method of Skraup and König gave the same cellobiose octacetate, the yield varying with the method of preparing the oxycelluloses.[3]

	Cellobiose Octacetate, Per Cent
Cellulose	25
"Hydralcellulose" (by H_2O_2)	25
Oxycellulose (by HNO_3)	16
Oxycellulose (by $KClO_3 + HCl$)	10
Acid cellulose (by precipitation with acid from Schweizer's solution)	7

Oxycellulose, formed by electrolysis of a potassium chloride solution containing cellulose, was more readily acetylated than normal cellulose, but the acetate contained less combined acetic acid. Acetolysis by Ost's method gave 30 to 31 per cent of crystalline cellobiose octacetate.[4]

Detection of Oxycellulose.—Many qualitative methods have been proposed for detecting oxycellulose. Most of them are based on the property of reduction, hence do not distinguish between oxycellulose and hydrocellulose. As the property of being dyed directly by basic dyestuffs, such as methylene blue, was not sufficiently well defined, it was proposed to use Fehling's solution, whereby fibers containing oxycellulose are colored

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[1] E. Knecht, *J. Soc. Dyers Colourists*, **38** (1922), 132.

[2] L. Vignon and F. Gerin, *Compt. rend.*, **131** (1900), 558.

[3] E. R. von Hardt-Stremayr, *Monatsh.*, **28** (1907), 73–78.

[4] R. Oertel, *Z. angew. Chem.*, **26** (1913), 246.

red by the cuprous oxide formed.[1] Nessler's reagent gives a gray color,[2] and Harrison's solution containing 1 per cent of silver nitrate, 4 per cent of sodium thiosulphate, and 4 per cent of sodium hydroxide, a gray to black color.[3]

Several methods depend upon the behavior of oxycellulose with dyes. Cotton spotted with oxycellulose is rinsed in acid, then many times with water, and dyed a deep shade with congo red. The cotton is then placed in sufficient acid to develop a blue color. On washing carefully with a limited amount of water until the ordinary cotton has a good red shade, the spots of oxycellulose will appear black on the red ground color.[4]

Oxidized cellulose develops a brown color proportional to its degree of oxidation when treated for 10 minutes with 750 cubic centimeters of an ice-cold solution containing 0.01 gram-molecule of tetrazotized benzidine and 80 cubic centimeters of normal sodium hydroxide. The reagent reacts to only a slight extent with hydrocellulose and not at all with normal bleached cotton, mercerized cotton, or with cotton so tendered with sulphuric acid as to have an increased affinity for methylene blue.[5]

Owing to its reducing properties, highly oxidized cellulose is able to fix flaventhrene directly, on boiling with $2N$ sodium hydroxide, by conversion of the dye to a blue vat.[6] On exposure to air, the blue color changes to yellow. Oxycellulose when boiled with direct cotton dyes, such as rosinduline 2B, and sodium hydroxide, destroys a large amount of the dye. Prolonged boiling removes the oxycellulose completely. The amount of dye destroyed can be determined by titration. Direct colors of the primuline type, that are unaffected by reducing agents, dye oxycellulose immediately.[7]

Oxycellulose has only a slight affinity for leucomethylene blue and may be distinguished in this way from cotton treated with dilute sulphuric acid, which has a marked affinity for it.[1] The affinity of the oxycellulose for a direct dye, such as diamine sky blue, may be restored by boiling it with dilute alkali.

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[1] M. Philip, *Z. öffentl. Chem.*, **6** (1900), 524; L. L. Lloyd, *J. Soc. Dyers Colourists*, **26** (1910), 273.

[2] H. Ditz, *J. prakt. Chem.*, **78** (1908), 343.

[3] W. Harrison, *J. Soc. Dyers Colourists*, **28** (1912), 361.

[4] A. B. Knaggs, *J. Soc. Dyers Colourists*, **24** (1908), 112.

[5] A. E. Everest and A. J. Hall, *J. Soc. Dyers Colourists*, **39** (1923), 47–49.

[6] R. Scholl, *Ber.*, **44** (1911), 1312.

[7] E. Knecht, *J. Soc. Dyers Colourists*, **37** (1921), 76–77.

The only qualitative tests characteristic of oxycellulose are those based on the activity of the carboxyl group. Oxycellulose gave a color reaction very similar to glucuronic acid by Tollens' napthoresorcinol method; it differed, however, in that the ether solution was colored reddish violet and no spectral bands were observed.[2] The test for glucuronic acid is carried out as follows:[3] Place in a small test tube about 20 milligrams of the substance to be examined, 5 to 6 cubic centimeters of water, 0.5 to 1.0 cubic centimeter of a 1 per cent solution of napthoresorcinol in alcohol, and 5 to 6 cubic centimeters of hydrochloric acid of sp. gr. 1.19. The mixture is warmed slowly to boiling, boiled for a minute, let stand 4 minutes, and cooled in running water. An equal volume of ether is then added and the contents shaken. The ether layer is colored blue or violet and shows a dark spectral band near the D line.

The reaction is not specific for glucuronic acid, but is given by a large number of substances containing aldehyde-carboxyl or keto-carboxyl groups.[4]

A useful test is that of Ditz[5] as amplified by Schwalbe and Becker.[6] In the presence of sodium chloride, the carboxyl group in oxycellulose turns methyl orange wine red. The cellulose to be examined is suspended in water; addition of a drop of methyl orange colors the liquid yellow or reddish yellow. On introducing a few cubic centimeters of a concentrated solution of sodium chloride, the color, in the presence of oxycellulose, changes to wine red; with other forms of cellulose there is practically no change. The method may be rendered quantitative by titration with standard alkali. Even here the distinction is not as sharp as might be desired.

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[1] E. Knecht and F. P. Thompson, *J. Soc. Dyers Colourists*, **37** (1921), 270–277.

[2] E. Heuser and F. Stöckigt, *Cellulosechemie*, **3** (1922), 70.

[3] B. Tollens, *Ber.*, **41** (1908), 1788; *cf. Ibid.*, 1783.

[4] J. A. Mandel and C. Neuberg, *Biochem. Z.*, **13** (1908), 148; C. Neuberg, *Ibid.*, **24** (1910), 436.

[5] H. Ditz, *Chem. Ztg.*, **31** (1907), 844.

[6] C. G. Schwalbe and E. Becker, *Ber.*, **54** (1921), 545.

Material	Corrected copper number	Cubic centimeters 0.01*N* alkali*	Color with methyl orange and NaCl
1. Oxycellulose (by bleaching powder)	10.99	41.4	Very strong rose
2. Nitrating cotton	0.28	1.8	Yellow
3. Wood pulp oxycellulose (by bleaching powder)	33.22	33.4	Rose
4. Wood pulp (for nitration)	1.00	4.1	Yellow
5. Oxycellulose (by $KMnO_4$)	8.03	27.7	Very strong rose
6. Oxycellulose (by H_2O_2)	5.80	10.4	Strong rose
7. Hydrocellulose (Girard)	3.64	4.6	Yellowish brown
8. Wood pulp, Ritter-Kellner, unbleached	1.14	7.0	Yellow
9. Wood pulp, normal bleach	2.14	7.1	Yellow
10. Wood pulp, overbleached	3.85	14.9	Yellow

* For 1 gram of material. Figures in this column are corrected for the alkalinity of the ash.

The "acid number" of Vieweg[1] shows that oxycellulose is more acid than hydrocellulose. This is obtained by boiling a weighed portion of the cellulose (3 grams) for 15 minutes with a measured quantity (200 cubic centimeters) of 0.5*N* sodium hydroxide and determining by titration the loss in alkalinity of a withdrawn portion of the liquor.

Formation of Furfural.—Oxycellulose on distillation with acids gives furfural.[2] Starch and sugars after oxidation with chromic acid gave as high as 11 per cent. Owing to the difficulty of isolating pentoses or obtaining a pentose reaction from many celluloses that gave furfural on acid distillation, Cross and Bevan assumed that they were natural oxycelluloses and contained "furfuroids." The best experimental evidence indicates that furfural is obtainable in quantity only from pentosans, under which subject the "natural oxycelluloses" are discussed in more detail.

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[1] W. Vieweg, *Papier-Ztg.*, **34** (1909), 1352.

[2] C. F. Cross, E. J. Bevan, and C. Beadle, *Ber.*, **26** (1893), 2520; **27** (1894), 1061, 1456.

In general, the more drastic the oxidation the smaller is the yield of oxycellulose and the greater the yield of furfural obtainable. The statement[1] that the acid distillate from oxycellulose gives a brownish-black methylfurfural phloroglucide completely soluble in cold 80 per cent alcohol, hence free from furfural phloroglucide, is open to question. It is much more probable, from the work of Cunningham and Dorée,[2] that hydroxymethylfurfural is formed. This aldehyde gives a red phloroglucide and methylfurfural a red-brown one. Oxycellulose obtained by the treatment of mercerized cotton with ozone gave 1.11 per cent of furfural and 0.66 per cent of hydroxymethylfurfural based on

FURFURAL FROM OXYCELLULOSE

Prepared with	Furfural, per cent	Author	Reference
CrO_3	4.1–8.2	CROSS, BEVAN, and BEADLE	*Ber.*, **26** (1893), 2522
$KClO_3 + HCl$	2.11–2.09	VIGNON	*Compt. rend.*, **126** (1898), 1356; **128** (1899), 1038
CrO_3	3.50–1.82	VIGNON	*Compt. rend.*, **126** (1898), 1356; **128** (1899), 1038
Bleached cotton	1.80–1.60	VIGNON	*Compt. rend.*, **126** (1898), 1356; **128** (1899), 1038
Alkaline NaOCl	1.79	VIGNON	*Compt. rend.*, **128** (1899), 1038
$Ca(OCl)_2$	2.6	TROMP DE HAAS and TOLLENS	*Ann.*, **286** (1895), 296
HNO_3 (wood)	7.0	VON FABER and TOLLENS	*Ber.*, **32** (1899), 2589
HNO_3 (cotton)	2.3 –3.2	VON FABER and TOLLENS	*Ber.*, **32** (1899), 2589
$Br_2 + CaCO_3$	1.4– 1.9	VON FABER and TOLLENS	*Ber.*, **32** (1899 , 2589
$Ca(OCl)_2$	1.09	NASTJUKOFF	*Ber.*, **33** (1900), 2237
$KMnO_4 + H_2SO_4$	1.09	NASTJUKOFF	*Ber.*, **33** (1900), 2237
Electrolysis of KCl	1.7	OERTEL	*Z. angew. Chem.*, **26** (1913), 246
$KClO_3 + HCl$	0.80	ZANOTTI	*Chem. Zentr.*, **70,** I (1899), 1209
$CrO_3 + H_2SO_4$	3.05	ZANOTTI	*Chem. Zentr.*, **70,** I (1899), 1209
$KMnO_4 + H_2SO_4$	1.90	ZANOTTI	*Chem. Zentr.*, **70,** I (1899), 1209
CrO_3	3.89	HEUSER and STÖCKIGT	*Cellulosechemie*, **3** (1922), 61
$Br_2 + CaCO_3$	2.1	HEUSER and STÖCKIGT	*Cellulosechemie*, **3** (1922), 61
H_2O_2	0.65	HEUSER and STÖCKIGT	*Cellulosechemie*, **3** (1922), 61
Ozone	1.1	CUNNINGHAM and DORÉE	*J. Chem. Soc.*, **101** (1912), 500

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[1] F. LENZE, B. PLEUS, and J. MÜLLER, *J. prakt. Chem.*, **101** (1920), 250.

[2] M. CUNNINGHAM and C. DORÉE, *Biochem. J.*, **8** (1914), 438.

the solubility of the mixed phloroglucides in alcohol. Hydroxymethylfurfural is formed more slowly and appears only in small amount as an impurity towards the end of the acid distillation.[1]

When oxidized cellulose is extracted with alkali, the portion precipitated by acidification of the alkaline filtrate gives an appreciably higher percentage of furfural than does the part insoluble in alkali or that not precipitated from the alkaline extract.[2] This indicates that the formation of furfural is directly linked up with the acid portion of the product.

The furfural distillate from oxycellulose prepared with chromic acid contains 13.8 per cent of substances behaving towards phloroglucinol like furfural. They are destroyed by redistillation of the hydrochloric acid distillate.[3]

α-, β-, and γ-Oxycelluloses and Their Salts.—The oxycelluloses prepared with bleaching powder and nitric acid have been called α- and β-oxycellulose, respectively.[4] Nastjukoff[5] has described a third form, γ-oxycellulose. The latter is obtained in yields of 60 to 80 per cent by heating the α-oxycelluloses, prepared with bleaching powder and potassium permanganate, with 5 per cent sulphuric acid for 3 and 1 hours, respectively, washing, then heating with 10 per cent sodium carbonate solution for 10 to 30 minutes at 70 to 100°. γ-Oxycellulose gives aqueous opalescent solutions that pass through filter paper and remain unaltered on standing or heating. Solutions of a concentration of 5 to 10 per cent resemble glycerine or viscose. Precipitation with acid renders it insoluble in water, but it becomes soluble again on treatment with sodium carbonate. It reduces Fehling's solution and gives a yellow hydrazone. The soluble form is the sodium salt of an acid giving on evaporation lustrous films that may be easily detached from glass. After drying at 80 to 100°, the salts of β-oxycellulose show decreased solubility in water, while those from α-oxycellulose are not affected.

When precipitated from alkaline solution with a salt or alcohol, β-oxycellulose was almost free from ash, hence contained little if any combined alkali.[1] β-Oxycellulose gave a barium salt containing about 5 per cent of barium, while the corresponding salt of γ-oxycellulose, prepared with bleaching powder, contained only 1 per cent of barium.[2]

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[1] E. Heuser and F. Stöckigt, *Cellulosechemie*, **3** (1922), 69.

[2] L. Vignon, *Compt. rend.*, **126** (1898), 1357.

[3] G. S. Fraps, *Am. Chem. J.* **25** (1901), 505.

[4] C. F. Cross and E. J. Bevan, *J. Soc. Chem. Ind.*, **3** (1884), 206.

[5] A. Nastjukoff, *Ber.*, **34** (1901), 719, 3589.

Oxidizing agents, according to Piest,[3] convert cellulose into α- and β-oxycellulose, the former being insoluble and the latter soluble in 5 per cent sodium hydroxide in the cold. The α-oxycellulose had all the properties of normal cellulose and should more correctly be considered as such. Cotton on boiling with 30 per cent sodium hydroxide dissolves partially, the portion going into solution being an acid cellulose.

Nastjukoff[4] has characterized the three forms of oxycellulose as follows:

1. α-Oxycellulose (Witz), insoluble in ammonia and dilute alkalis.
2. β-Oxycellulose, soluble in ammonia.
3. γ-Oxycellulose, soluble in ammonia and the fixed alkalis, and in water as well.

According to Bancroft,[5] there is no justification for assuming the existence of three oxycelluloses. It is most probable that α-oxycellulose is unchanged cellulose and that oxycellulose consists of cellulose contaminated with various oxidation products. Regardless of the oxidizing agents employed, the resulting products have the following characteristics:

1. No change in color when heated in air to 100°.
2. They form a gelatinous mass when warmed with water.
3. They are partially soluble in KOH or NaOH with a yellow color.
4. They dissolve readily in water, after precipitation from alkaline solution with alcohol or acid, followed by dialysis.
5. They reduce Fehling's solution, but this property is lost by too long heating.

One must agree with Bancroft that no pure oxycellulose has been prepared as yet. As will be shown elsewhere, the structure of cellulose renders this end extremely difficult of attainment.

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[1] C. F. Cross and E. J. Bevan, *J. Chem. Soc.*, **43** (1883), 22.

[2] A. Nastjukoff, *Ber.*, **34** (1901), 3590.

[3] C. Piest, *Z. angew. Chem.*, **26** (1913), 27.

[4] A. Nastjukoff, *Ber.*, **34** (1901), 720, 722, 3590.

[5] W. D. Bancroft, *J. Phys. Chem.*, **19** (1915), 159–168.

Composition of Oxycellulose.—Nastjukoff[1] believed that the oxycellulose of Witz consisted of a mixture of cellulose and oxycellulose. On heating with strong caustic soda by Lange's method,[2] there remained a residue of 64.5 to 69.4 per cent of cellulose. The residue from the treatment of oxycellulose with alcoholic sodium hydroxide is a hydrated cellulose.[3]

According to Tollens,[4] oxycelluloses are mixtures, or, rather, chemical combinations, of cellulose with a more highly oxygenated body, $C_6H_{10}O_6$ or $C_6H_8O_6$, termed "celloxin." The latter is the true oxycellulose not yet isolated. When 30 grams of oxycellulose were boiled with lime water, there remained 23.5 grams of a material having all the properties of a pure cellulose.[5] As a result of fusing oxycellulose (by HCl and $KClO_3$) with potassium hydroxide at 180°, Vignon[6] concluded that it contained 75 per cent of oxycellulose and 25 per cent of cellulose. Strong solutions of the alkalis decompose oxycellulose into cellulose and a soluble acid.[7] Schwalbe and Becker[8] remove the degradation products from cellulose by boiling with the alkaline earths. In this way, an oxycellulose prepared with bleaching powder left a 60 per cent residue consisting of practically pure cellulose.

Oxycellulose consists of a mixture of cellulose, hydrocellulose, and their oxidation products.[9] According to Harrison, it consists of adsorption compounds of peptized cellulose and reducing substances.[10]

Nature of Oxycellulose.—There is much evidence for the presence of aldehyde groups in oxycellulose. Witz[11] observed that oxycellulose as well as its alkaline solution had a strong reducing action on Fehling's solution, while hydrocellulose had

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[1] A. Nastjukoff, *Bull. Mulhouse*, **62** (1892), 493–510.

[2] G. Lange, *Z. physiol. Chem.*, **14** (1890), 286.

[3] A. Nastjukoff, *Ber.*, **33** (1900), 2237.

[4] O. von Faber and B. Tollens, *Ber.*, **32** (1899), 2589.

[5] J. J. Murumow, J. Sack, and B. Tollens, *Ber.*, **34** (1901), 1431.

[6] L. Vignon, *Compt. rend.*, **125** (1897), 449.

[7] L. Vignon, *Compt. rend.*, **131** (1900), 708.

[8] C. G. Schwalbe and E. Becker, *J. prakt. Chem.*, **100** (1919), 19.

[9] V. Zanotti, *Chem. Zentr.*, **70,** I (1899), 1209.

[10] W. Harrison, *J. Soc. Dyers Colourists*, **28** (1912), 360.

[11] G. Witz, *Bull. Rouen*, **11** (1883), 219; C. F. Cross and E. J. Bevan, *Chem. News*, **64** (1891), 63.

FORMULÆ FOR OXYCELLULOSE

Oxidizing agent	C, per cent	H, per cent	O, per cent	Formula	Author	Reference
Bleaching powder.....	43.63	5.99	50.38	$C_{24}H_{20}O_{21}$	WITZ	*Bull. Rouen*, **10** (1882), 447
Nitric acid...........	43.34	5.28	51.38	$C_{18}H_{26}O_{16}$	CROSS and BEVAN	*J. Chem. Soc.*, **43** (1883), 22
$KClO_3 + HCl$........	43.40	5.90	50.70	$C_{24}H_{40}O_{21}$	VIGNON	*Compt. rend.*, **136** (1903), 898
Nitric acid...........	43.41	6.19	50.40	$C_{36}H_{60}O_{31}$	LINDSEY and TOLLENS	*Ann.*, **267** (1892), 366
Nitric acid...........	42.32	6.05	51.63	$C_{18}H_{30}O_{16.5}$	FLINT and TOLLENS	*Ann.*, **272** (1893), 288
Nitric acid (A)........	43.59	6.05	50.36	$C_{30}H_{48}O_{26}$	VON FABER and TOLLENS	*Ber.*, **32** (1899), 2594
Nitric acid (B)........	43.35	5.89	50.76	$C_{24}H_{38}O_{21}$	VON FABER and TOLLENS	*Ber.*, **32** (1899), 2594
$Br + CaCO_3$..........	42.15	6.13	51.72	$C_{12}H_{20}O_{11}$	VON FABER and TOLLENS	*Ber.*, **32** (1899), 2592
Bleaching powder.....	.....	....	.....	$C_6H_{10}O_6$	NASTJUKOFF	*Bull. Mulhouse*, **62** (1892), 510
$KClO_3 + HCl$........	43.66	6.60	49.74	....	ZANOTTI	*Chem. Zentr.*, **70,** I (1899), 1209
$CrO_3 + H_2SO_4$........	42.96	6.52	50.52	....	ZANOTTI	*Chem. Zentr.*, **70,** I (1899), 1209
$KMnO_4 + H_2SO_4$.....	42.52	6.56	50.92	....	ZANOTTI	*Chem. Zentr.*, **70,** I (1899), 1209
Nitric acid...........	41.92	6.27	51.81	....	BULL	*J. Chem. Soc.*, **71** (1897), 1093
Hydrogen peroxide....	43.8	6.2	50.00	$C_{36}H_{60}O_{31}$	BUMCKE and WOLFFENSTEIN	*Ber.*, **32** (1899), 2501

a feeble one. In addition to reducing Fehling's solution, it colors Schiff's reagent easily and intensely.[1]

Oxycellulose contains aldehydic or ketonic oxygen, since it reacts with phenylhydrazine.[2] The osazones prepared from the oxycelluloses from cotton, flax, hemp, and ramie were considered to be identical. They contained 1.58 to 1.69 per cent of nitrogen.[3] Vignon[4] found that the greater the degree of oxidation, the greater the amount of nitrogen fixed by the oxycellulose when boiled with phenylhydrazine. Acid oxidizing agents are preferable, since alkaline ones largely destroy the reducing products as formed.

Oxycellulose prepared with	Nitrogen fixed, per cent	Corresponding phenylhydrazine, per cent
$KClO_3 + HCl$	2.06	7.94
NaOCl (alkaline; boiling)	0.87	3.37
$K_2Cr_2O_7 + H_2SO_4$:		
a. 48 hours in the cold	1.82	7.03
b. 120 hours in the cold	2.00	7.71
c. 1 hour, boiling	2.20	8.48

Oxycellulose, like the aldehyde sugars, gives color reactions with phenols in the presence of sulphuric acid: with α-napthol, violet; with β-napthol, brown; and with thymol, rose.[5]

The various oxycelluloses show marked differences in the yield of furfural, resistance to alkalis, acidity, and reducing properties.[6] In one class of oxycelluloses the acid, in the other the aldehyde, character predominates. In hydrocellulose the acid property is almost entirely absent. Denitrated wood cellulose and Chardonnet artificial silk show the combined properties of oxycellulose and hydrated cellulose, the former showing chiefly the character of an oxycellulose, the latter that of hydrated cellulose.

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[1] E. R. Flint and B. Tollens, *Ann.*, **272** (1893), 289; L. Vignon, *Compt. rend.*, **125** (1897), 448.

[2] A. Nastjukoff, *Bull. Mulhouse*, **62** (1892), 510; A. Scheurer and E. Nölting, *Ibid.*, p. 492.

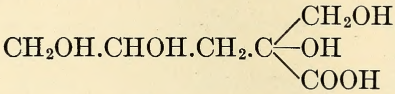
[3] L. Vignon, *Compt. rend.*, **131** (1900), 558.

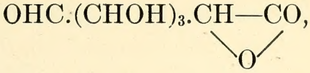
[4] L. Vignon, *Compt. rend.*, **128** (1899), 1038.

[5] E. Jandrier, *Compt. rend.*, **128** (1899), 1407.

[6] C. G. Schwalbe and E. Becker, *Zellstoff u. Papier*, **1** (1921), 100–103, 135–139.

Oxycellulose when heated with lime water gave isosaccharinic acid and dihydroxybutyric acid.[1] No very definite conclusions can be drawn from this reaction, however, since several carbohydrates, including hydrocellulose, give these products. Tollens[2] concluded that oxycellulose contained a carboxyl group and an aldehyde or ketone group, since it formed osazones and reduced Fehling's solution.

Glucose, on treatment with lime water, gives metasaccharinic acid, $CH_2OH.[CHOH]_2.CH_2.CHOH.COOH$, and not isosaccharinic acid,  $CH_2OH.CHOH.CH_2.C\begin{array}{l}\diagup CH_2OH\\ -OH\\ \diagdown COOH\end{array}$. Since isosaccharinic acid has apparently been obtained only from lactose and maltose, Pringsheim[3] concludes that the formation of this acid is limited to a glucose group having a glucosidal linkage. If cellobiose should be shown to give isosaccharinic and not metasaccharinic acid, it would be certain proof that the isosaccharinic acid was formed from the oxycellulose or hydrocellulose before the rupture of the glucosidal linkage at the aldehyde group of the glucose residues. He believes that oxycelluloses consist of a mixture of anhydrocellobiose and cellobionic acid held together by secondary valencies. Hintikka[4] has found that cellobiose does give isosaccharinic acid with lime water.

Vignon[5] found that the apparent acidity of oxycellulose was much greater than for cellulose. On immersing these substances in normal potassium hydroxide, the heats liberated for 100 grams of material were 1.30 and 0.74 calories respectively. When oxycellulose nitrate was dissolved in potassium hydroxide, oxypyruvic acid was isolated as the osazone from the decomposition products.[6] Since this compound had been previously obtained from cellulose nitrate by Will,[7] Vignon concluded that oxycellulose might be formed during nitration. In his opinion, the essential group in oxycellulose is  $OHC.(CHOH)_3.CH{-}CO$ (bridged by O), this being at once an aldehyde, alcohol, and lactone of an acid, $C_6H_{10}O_7$. The formation of oxypyruvic acid and furfural takes place as follows:

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[1] O. von Faber and B. Tollens, *Ber.*, **32** (1899), 2596.

[2] B. Tollens, *Ber.*, **34** (1901), 1435.

[3] H. Pringsheim, *Cellulosechemie*, **2** (1921), 61.

[4] S. V. Hintikka, C. A., **17** (1923), 3486.

[5] L. Vignon, *Compt. rend.*, **125** (1897), 448.

[6] L. Vignon, *Compt. rend.*, **127** (1898), 872.

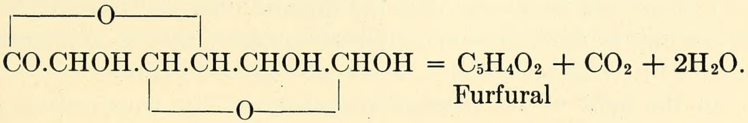
[7] W. Will, *Ber.*, **24** (1891), 400.

$$C_6H_{10}O_7 + O_2 = \underset{\text{Oxypyruvic Acid}}{2\,CHOH.CO.COOH} + H_2O.$$

$$C_6H_{10}O_7 = \underset{\text{Furfural}}{C_5H_4O_2} + 3H_2O + CO_2.$$

Berl and Fodor[1] support the view that cellulose nitrates are really esters of oxycellulose. The latter contain glucosidohexonic acids, Tollen's "celloxin" being the lactone form of the hexonic acid, cellonic acid. Cellulose nitrate,[2] on hydrolysis with a 30 per cent solution of alcoholic potassium hydroxide, gave oxalic and pyruvic acids but no saccharic acid; with 10 per cent aqueous potassium hydroxide, oxalic, malic, glycollic, trihydroxyglutaric, dihydroxybutyric, malonic, and tartronic acids were obtained.

The lactone of glucuronic acid, $C_6H_8O_6$, gives, in addition to furfural, 25 per cent of carbon dioxide, the latter being suitable for its quantitative determination.[3]



$$CO.CHOH.CH.CH.CHOH.CHOH = \underset{\text{Furfural}}{C_5H_4O_2} + CO_2 + 2H_2O.$$

Glucuronic acid lactone

It was shown by Heuser and Stöckigt[4] that oxycellulose actually contains a group related to, if not identical with, glucuronic acid. This explains the formation of furfural and carbon dioxide when oxycellulose is distilled with 12 per cent hydrochloric acid. Oxycellulose prepared with chromic acid gives the highest yields of furfural and carbon dioxide. The yields of carbon dioxide from various carbohydrates were:

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[1] E. Berl and A. Fodor, *Z. Schiess-u. Sprengstoff.*, **5** (1910), 254, 269.

[2] E. Berl and A. Fodor, *Z. Schiess-u. Sprengstoff.*, **5** (1910), 296, 313.

[3] K. U. Lefèvre and B. Tollens, *Ber.*, **40** (1907), 4517.

[4] E. Heuser and F. Stöckigt, *Cellulosechemie*, **3** (1922), 61.

	CO_2 Per Cent
Glucose	0.04
Pure cotton	0.026
Hydrocellulose	0.04
Sulphite pulp (unbleached)	0.08
Sulphite pulp (bleached)	0.24
Soda pulp (bleached)	0.22
Oxycellulose (by chromic acid)	1.53
Glucuronic acid lactone	24.84

Even though glucose on prolonged heating with dilute mineral acids gives from 1.5 to 2.0 per cent of carbon dioxide,[1] the formation of furfural and carbon dioxide under the conditions specified must be considered as characteristic of oxycellulose.

It was found that by heating the crude oxycellulose with 1 per cent sulphuric acid under pressure, it was possible to remove the small portion giving furfural and carbon dioxide. The residue was hydrocellulose. The hydrolyzed portion gave an impure, unstable barium salt related to glucuronic acid. A reddish-violet color was obtained by the β-napthoresorcinol test, but the ether solution showed no spectral bands. The oxycellulose, on hydrolysis with strong hydrochloric acid, gave only 10 per cent less glucose than pure cellulose.[2]

Tollens[3] has suggested that the furfural obtained from oxycellulose may be derived from certain groupings related to glucosone, $CH_2OH.[CHOH]_3.CO.CHO$, which also gives furfural.[4]

In the light of our present knowledge of the constitution of cellulose, the degradation of cellulose to glucuronic acid, with the intermediate formation of oxycellulose, must take place in several stages. In the glucose anhydride units shown below, the dashes represent oxygen linkages. The first step involves the oxidation of the primary alcohol group A to the aldehyde B; the next being the oxidation of the latter to the carboxyl group C. Hydrolysis then gives glucuronic acid D.

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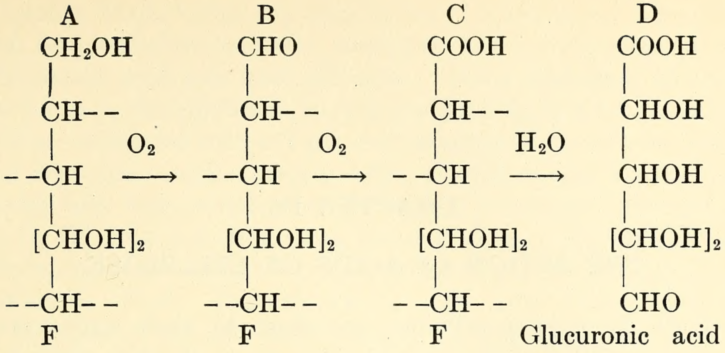
[1] M. Berthelot and G. André, *Compt. rend.*, **123** (1896), 567.

[2] E. Heuser and F. Stöckigt, *l.c.*, 64.

[3] B. Tollens, *Ann.*, **286** (1895), 301.

[4] E. Fischer, *Ber.*, **22** (1889), 93.



The grouping CF would represent the true "oxycellulose," however inappropriate the nomenclature of the latter. It is highly improbable that more than a small amount of CF could be formed, since all known oxidizing agents appear to affect cellulose profoundly. The alkaline agents rapidly produce total disintegration, while oxidation in the presence of acids produces simultaneous hydrolysis. Even hydrogen peroxide hydrolyzes the cellulose molecule.

The reducing action of oxycellulose may be due to both the aldehydic group B formed by oxidation and to that resulting from hydrolysis at the glucosidal linkage at F. According to the course of the reaction, an oxycellulose may be pronouncedly aldehydic or acid, but it will have both properties. It will, obviously, be extremely difficult to control the oxidation so as to obtain a uniform product.

CHAPTER IX

THE ACTION OF ACIDS ON CELLULOSE

Acids decompose cellulose according to their nature and strength. Dilute acids at the boiling point, or when allowed to dry on the fibers, produce chiefly hydrocellulose. Under more drastic conditions, hydrolysis proceeds to dextrins and the simple sugars. Oxidizing acids give both hydrocellulose and oxycellulose, and finally the simple aliphatic acids. Under certain conditions, acids may cause hydrolysis to the simple sugars, followed by dehydration to furfural and hydroxymethylfurfural.

Hydrocellulose.—Hydrocellulose is an indefinite product consisting of small amounts of bodies of the nature of dextrins associated with unchanged cellulose. Fibers which have been converted to hydrocellulose are characterized by brittleness and the presence of aldehyde groups. The absence of carboxyl groups distinguishes it from oxycellulose.

The effect of dilute mineral acids in decreasing the strength of linen was pointed out by Kolb[1] in 1868. A few years later Girard[2] described a modification of cellulose, obtained by the action of mineral acids of moderate concentration, and called by him hydrocellulose. The latter was obtained by immersing cotton in sulphuric acid of 45° Bé. (55 per cent) for 12 hours, or by impregnating the fiber with very dilute acid and heating at 100°. The product reduced Fehling's solution and dissolved, on heating in dilute potassium hydroxide solution, to a strongly colored liquid with reducing properties. The friability of paper from which bleaching powder had not been completely removed was attributed to hydrocellulose formed by the hydrochloric and hypochlorous acids set free by the carbon dioxide of the air.

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[1] J. Kolb, *Bull. Mulhouse*, **38** (1868), 922.

[2] A. Girard, *Compt. rend.*, **81** (1875), 1105–1108.

Cotton, linen, wood, and other forms of cellulose are converted into hydrocellulose by nitric, sulphuric, and hydrochloric acids.[1] Phosphoric acid acts with difficulty. Moist hydrogen chloride gas forms hydrocellulose in an hour; on heating, in a few minutes. Cotton, saturated with a 1 per cent solution of the mineral acids and the excess acid removed, when allowed to air dry, is converted into hydrocellulose at the end of 3 months. Heated to 60 to 70°, the transformation takes place in a few hours. At this temperature an acid of a concentration of 0.001 per cent has a noticeable effect. The chlorides of zinc, iron, and aluminum at 80° convert cellulose into white hydrocellulose. The conversion loss is about 10 per cent.

Hydrocellulose differs from ordinary cellulose in the following ways. When heated in a sealed tube at 160° with 10 parts of 1 per cent potassium hydroxide solution, it is rendered completely soluble, while ordinary cellulose is unchanged. On heating in a sealed tube with 5 per cent sulphuric acid at 180° for 5 to 6 hours, cellulose dissolves entirely with a slight coloration and no formation of gas, while hydrocellulose gives a carbonaceous deposit and a noticeable quantity of gaseous products. Hydrocellulose acetylates readily, being converted into a viscous syrup by boiling under a reflux condenser with acetic anhydride; cellulose is not affected. Pyroxylins made from hydrocellulose are very brittle, the nitration proceeding, however, to the same extent as with cotton. The prominent physical characteristics of hydrocellulose are friability and adhesive properties.[2]

Cotton exposed to the vapors of hydrochloric acid and nitric acid (36° Bé.) decreased in strength from 24.3 to 9.6, and from 24.3 to 18.7 respectively, after exposure for 40 minutes. The more pronounced effect of hydrochloric acid is due to its greater vapor pressure.[3]

Dilute nitric acid at ordinary temperatures gradually changes cellulose to hydrocellulose.[4]

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[1] A. Girard, *Ann. chim. phys.*, [5] **24** (1881), 337–384; *Bull. Soc. d'Encourg.*, [3] **9** (1882), 176–198.

[2] A. Girard, *l.c.*

[3] A. Scheurer, *Bull. Mulhouse*, **58** (1888), 363.

[4] C. Haeussermann, *Z. angew. Chem.*, **23** (1910), 1761; **26** (1913), 456; Guichard, *Bull. soc. chim.*, **7** (1892), 559.

According to Lester,[1] cotton containing 0.01 per cent of hydrochloric acid shows no appreciable "tendering" after drying with a hot iron and heating in a water oven for 1.5 hours. Cotton, tendered by treatment with dilute sulphuric acid and drying without heat, gained in strength by neutralization of the acid and by mercerization.[2] Cohen[3] found that the loss in strength on tendering corresponded with the increase of the copper number. Hydrochloric acid must have a strength of at least 0.008 per cent and sulphuric acid 0.033 per cent when boiled with cotton to produce an increase in its copper number. Cotton soaked in the dilute acid in the cold, dried, then heated for 10 minutes at 120° is affected by hydrochloric acid of 0.002 per cent and sulphuric acid of 0.008 per cent.

The loss of strength of cotton boiled with dilute acids of the same normality runs approximately parallel with the relative conductivities of the acids.[4]

The tendering of cotton dyed with sulphide colors is due to the action of sulphuric acid formed by atmopheric oxidation.[5]

Organic Acids.—Calvert[6] treated linen and cotton fibers with 2 to 4 per cent solutions of tartaric, citric, and oxalic acids, and after air drying, heated them at 80, 100, and 126°. No appreciable loss in strength was obtained except with oxalic acid at 126°. Cotton saturated with 5 per cent solutions of oxalic, tartaric, and citric acids, and heated at 100°, is completely changed into hydrocellulose by the former, while tartaric acid has less action, and citric acid the least.[7]

Scheurer[8] studied the effect of dilute solutions of oxalic, lactic, tartaric, citric, thiocyanic, orthophosphoric, metaphosphoric, pyrophosphoric, and phosphorous acids on cotton under the influence of hot air and steam. Of these acids, thiocyanic produced the greatest decrease in strength in air at 40 to 50°.

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[1] J. H. Lester, *J. Soc. Chem. Ind.*, **34** (1915), 934–936.

[2] H. Wilkinson, *J. Soc. Dyers Colourists*, **33** (1917), 148–151.

[3] M. Cohen, *J. Soc. Dyers Colourists*, **31** (1915), 162–165; *cf.* W. A. Lawrance, *Can. Chem. J.*, **3** (1919), 329–331.

[4] M. Fort and F. Pickles, *J. Soc. Dyers Colourists*, **31** (1915), 255–260.

[5] J. E. Pilling, *J. Soc. Dyers Colourists*, **22** (1906), 54–65; G. E. Holden, *Ibid.*, **26** (1910), 76–78; E. Vlies, *Ibid.*, **26** (1910), 79–81; W. Ebbers, *Z. Farben-und Textilchem.*, **1** (1902), 92; T. R. Appleyard and T. B. Deakin, *J. Soc. Dyers Colourists*, **18** (1902), 128.

[6] F. C. Calvert, *Bull. Mulhouse*, **29** (1858), 208–213; *cf.* J. A. Barral and Salvetat, *Ann. chim. phys.*, [5] **9** (1876), 129.

[7] A. Girard, *l.c.*; G. E. Pilkington, *J. Soc. Dyers Colourists*, **31** (1915), 149.

[8] A. Scheurer, *Bull. Mulhouse*, **74** (1904), 211.

Under the usual conditions of half-wool dyeing and finishing, acetic and formic acid reduce the tensile strength of cotton about one-half.[1]

In time, oxalic acid converts cellulose to hydrocellulose even at the ordinary temperature. When cellulose containing oxalic acid is heated in the dry state, apparently a small portion of the acid combines to form an ester.[2]

When heated at 100° with 8 to 16 per cent solutions of oxalic acid for 2.5 to 12 hours, viscose yields 97 to 98 per cent of hydrocellulose.[3] The latter has a copper number of 10.47 to 10.83 and is completely soluble in 8 per cent sodium hydroxide. The hydrocellulose obtained from cotton in this way is only partially soluble in 10 per cent sodium hydroxide. When heated with a 5 per cent solution of oxalic acid at 180° for 30 minutes, viscose hydrocellulose gave 11.86 per cent of hydroxymethylfurfural, in comparison with 5.74 per cent from viscose itself, and 0.81 per cent from ordinary cotton.

Salts.—Salts producing acids by hydrolysis likewise form hydrocellulose. Girard[4] observed that the chlorides of zinc, iron, and aluminum at 80° convert cellulose into white hydrocellulose. Barral and Salvetat[5] tried various salts as carbonizing agents. The fibers were saturated with salt solutions of 5° Bé. and heated in an oven at 140° for 30 minutes.

	Remarks
Chlorides of Na, K, NH_4, Ba, Hg	No effect
Chlorides of Ca, Mg	Slightly brittle
Chlorides of Fe, Sn, Zn, Cu	Black and brittle
Nitrates of Pb, Na, K, Ca, Ba, NH_4	No effect
Nitrates of Mg, Fe, Ag	Brittle
Sulphates of Cu, NH_4, Mn, Fe, Ca, Mg, Na, K	No effect
Sulphate of Zn	Slight
Sulphates of Sn, Al	Pronounced

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[1] W. Zänker and O. Mann, *Färber-Ztg.*, **27** (1916), 355.

[2] J. F. Briggs, *J. Soc. Chem. Ind.*, **31** (1912), 520–522.

[3] E. Heuser and F. Eisenring, *Cellulosechemie*, **4** (1923), 25.

[4] A. Girard, *Ann. chim. phys.*, [5] **24** (1881), 337.

[5] J. A. Barral and Salvetat, *Ann. chim. phys.*, [5] **9** (1876), 126–131.

Preparation.—According to Ost,[1] a hydrocellulose with constant properties is best obtained by treating 5 grams of cotton with 40 grams of glacial acetic acid and 2 grams of concentrated sulphuric acid, and allowing the mixture to stand at room temperature for 2 days. Jentgen[2] treated 10 grams of cellulose with 300 cubic centimeters of glacial acetic acid and 2 cubic centimeters of hydrochloric acid, at the boiling point, for 10 to 15 minutes. When sulphuric acid is substituted for the latter, the conversion is rapid, but the hydrocellulose has a tendency to gelatinize on washing.

Hydrocellulose may be obtained by melting ferric chloride, $FeCl_3.6H_2O$, at a low heat and gradually adding absorbent cotton in an amount such that the resulting solution does not become too thick. On pouring into water, a precipitate of finely divided hydrocellulose is obtained.[3] It is difficult to free the precipitate from iron.

Tollens[4] prepared hydrocellulose by treating cellulose with sulphuric acid of sp. gr. 1.52 to 1.54 (61.6 to 63.4 per cent) for 10 to 48 hours. Acid of the strength used by Girard (55 per cent) was not sufficiently strong. The products, most strongly attacked, reduced Fehling's solution slightly and were gelatinized by washing with water. Strong sodium hydroxide solution also gelatinized the hydrocellulose and partly dissolved it. Iodine solution gave only a weak coloration, but zinc chloriodine a deep blue. Heating with 3 per cent sulphuric acid on the water bath for 8 hours dissolved only a little of the hydrocellulose, hence only a small amount of reducing sugar was formed.

Seidel,[5] by the action of dry hydrogen chloride on sulphite cellulose, obtained a friable powder similar to the "acid cellulose" of Bumcke and Wolfenstein.[6] It dissolved readily in 10 per cent sodium hydroxide, from which solution it was precipitable with acids. Evidently, either the cellulose or the hydrogen chloride was not dry. Girard found that the dry gas was without action.

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[1] H. Ost, *Z. angew. Chem.*, **19** (1906), 994.

[2] H. Jentgen, *Z. angew. Chem.*, **23** (1910), 1543; *cf.* C. G. Schwalbe, *Ibid.*, 438.

[3] Z. Northrup, *Abstracts Bact.*, **3** (1919), 7.

[4] J. J. Murumow, J. Sack, and B. Tollens, *Ber.*, **34** (1901), 1431.

[5] H. Seidel, *Chem. Zentr.*, **71,** I (1900), 443.

[6] G. Bumcke and R. Wolfenstein, *Ber.*, **32** (1899), 2493.

When moisture is rigidly excluded, the gas is absorbed by the cellulose, but the latter can be recovered practically unchanged by subsequent washing with water.[1] Dry hydrogen chloride is very slow in its action, but solutions of the gas in anhydrous alcohol, ether, and benzene have appreciably greater tendering action than aqueous solutions of the same concentration.[2] Perhaps in this case prolonged contact formed water by dehydration of the cellulose.

Cellulose, when heated at a temperature of 60 to 70° with glacial acetic acid containing free chlorine, gives a hydrocellulose whose acetyl derivatives are characterized by a high solubility in water and alcohol.[3]

A product of considerable interest is the "alkali-soluble cellulose" of Knoevenagel.[4] It is prepared by the various methods resulting in the formation of hydrocellulose, but only a modified cellulose can be used. Preferably, viscose cellulose containing 11.5 per cent of moisture is subjected to the action of hydrogen chloride gas for 12 hours. Dry cellulose does not react and the duration of the acid treatment depends upon the amount of moisture in the cellulose. The product from viscose is completely soluble in the cold in 8 per cent caustic soda, while that from cellulose regenerated from cellulose acetate is only about one-tenth as soluble. From the alkaline solution, acids precipitate it quantitatively.

A suitable modified cellulose was also prepared by heating sulphite pulp in an indifferent solvent, such as glycerine and xylene, a certain amount of moisture being essential for the reaction. It had been found by Glum[5] that cellulose, when heated above 100° in stable liquids, such as glycerine and oil, is so modified that it is about twice as soluble as ordinary cellulose in the usual cellulose solvents, the same being true of the solubility, in appropriate solvents, of the derivatives of the modified cellulose. Sulphite pulp, heated in xylene for 6 hours at 140°, gave, after the acid treatment, a product of which 94 per cent was soluble in cold 8 per cent caustic soda.[1]

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[1] H. Jentgen, *Z. angew. Chem.*, **23** (1910), 1544.

[2] H. F. Coward, F. C. Wood, and F. L. Barrett, *J. Textile Inst.*, **14** (1923), 520.

[3] "Fabrik Chemischer Preparate von R. Sthamer," G. P. 123121 (1900).

[4] E. Knoevenagel and H. Busch, *Cellulosechemie*, **3** (1922), 42–60.

[5] O. Glum & Co., G. P. 217316 (1909).

Alkali-soluble cellulose is easily soluble in cellulose solvents, but insoluble in ammonia and water. It is stained bluish violet by zinc chloriodine and iodine (KI + I) solutions, the coloration being only slowly removed by washing with water. It is stable at 100°. No coloration is obtained with Schiff's reagent. On heating with milk of lime, alkali-soluble cellulose loses from 40 to 50 per cent in weight, but the copper number of the residue (13.0) is practically the same as that of the original (14.0).

In the opinion of Heuser,[2] Girard's hydrocellulose is a mixture of cellulose and hydrocellulose, while Knoevenagel's "alkali-soluble cellulose" is the true hydrocellulose. The latter behaves as a uniform product and gives uniform derivatives on acetylation and methylation. Methylation gives dimethylhydrocellulose, $[C_{12}H_{16}O_6.(OCH_3)_4]_2$, which is a dimethyl derivative of a dimeric anhydrocellobiose.[3]

Hess,[4] who examined Knoevenagel's hydrocellulose in cuprammonium solution, states that it is a mixture. The specific rotation of the product varied with the time of exposure to hydrochloric acid vapors.

Alkali hydrocellulose of the composition $C_{12}H_{20}O_{10}.2NaOH$ is obtained by dissolving viscose hydrocellulose in strong sodium hydroxide and preciptating with alcohol.[5]

It has been maintained by Jentgen[6] that the hydrolysis of cellulose, *e.g.*, the formation of hydrocellulose, is produced only by acids and salts in their molecular state, and not by the ionized portion, as is generally assumed. He heated cellulose in solvents in which the catalysts could be finely distributed in the molecular state, as in glacial acetic acid, ether, and various esters. Hydrolysis cannot take place without the presence of water, but the catalysts are adsorbed by the cellulose and simply act as contact agents. A 1 per cent aqueous solution of an acid hydrolyzes cellulose very slowly, while with a non-dissociating solvent the hydrolysis proceeds rapidly. This point of view has been protested by Schwalbe.[1]

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[1] E. Knoevenagel and H. Busch, *Cellulosechemie*, **3** (1922), 42–60.

[2] E. Heuser and W. von Neuenstein, *Cellulosechemie*, **3** (1922), 89–96, 101-107.

[3] E. Heuser and G. Jayme, *Ber.*, **56** (1923), 1242–1243.

[4] K. Hess, *Ann.*, **435** (1924), 142.

[5] E. Heuser and F. Eisenring, *Cellulosechemie*, **4** (1923), 25.

[6] H. Jentgen, *Z. angew. Chem.*, **23** (1910), 1541–1546; **24** (1911), 11–12, 585–586.

Properties of Hydrocellulose.—Perhaps as a result of a qualitative test only, Vignon[2] incorrectly concluded that hydrocellulose had no action on Fehling's solution. This led him to the further assumption that the product obtained by the denitrification of cellulose nitrate with ammonium sulphide was either cellulose or hydrocellulose, since it had no reducing action.[3]

Hydrocelluloses, according to Schwalbe,[4] have a high copper number, a low hygroscopic moisture content, a weak affinity for basic dyes, and a considerable solubility in the caustic alkalis. They are stained blue by zinc chloriodine, but the color is readily removed by washing with water. Some properties of the hydrocelluloses prepared by him are given above. It will be noted that the copper numbers vary from 4.0 to 8.8; Bay[5] obtained 3.06 to 4.69 for hydrocelluloses prepared by Girard's method, using 3 per cent sulphuric acid, while Qvist[6] gives 4.3

Hydrocellulose from	Copper number	Hygroscopic water, per cent
1. Cotton satin dissolved in concentrated H_2SO_4 and precipitated with water	7.9	5.3
2. Cotton satin with H_2SO_4 of 45° Bé	3.9	6.3
3. Cotton satin with HCl gas	4.0	3.8
4. Filter paper with HCl gas	5.6	1.2
5. Cotton satin with 3 per cent H_2SO_4	5.6	3.6
6. Absorbent cotton with 3 per cent H_2SO_4	5.2	
7. Filter paper with 3 per cent H_2SO_4	6.2	3.8
8. Parchment paper with 3 per cent H_2SO_4	8.7	6.0
9. Mercerized cotton with 3 per cent H_2SO_4	8.8	6.3

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[1] C. G. Schwalbe, *Z. angew. Chem.*, **23** (1910), 2030; **24** (1911), 12.

[2] L. Vignon, *Compt. rend.*, **131** (1900), 708.

[3] L. Vignon, *Compt. rend.*, **131** (1900), 530.

[4] C. G. Schwalbe, *Z. angew. Chem.*, **20** (1907), 2166; *Ber.*, **40** (1907), 4523.

[5] C. Bay, "Zur Kenntnis der Hydro-, Oxy-, Hydral-, und Acidcellulosen," Diss. Giessen (1913), p. 32.

[6] W. Qvist, *Papier-Fabr.*, **17** (1919), 820.

to 5.1 for hydrocelluloses from sulphite pulp. Knoevenagel's hydrocellulose[1] had a copper number of about 12.5, while Heuser[2] obtained 10.47 to 10.83 for a similar product.

A β-series of hydrocelluloses, obtained by the aging of alkali cellulose, has been described by Cross and Bevan.[3] The "hydrocellulose" formed a microscopically fine powder. It had high hygroscopicity, was without reducing action, and was comparatively stable towards certain esterifying processes. Apparently, the only reason for classifying the compound as a hydrocellulose was its state of division. This is insufficient.

Hydrocellulose	α-Series by action of acids	β-Series by action of alkalis
Hygroscopic moisture	3.5–5.0 per cent	8–11 per cent
Action of Fehling's solution	Reducing	Non-reducing

The hygroscopic moisture content of hydrocellulose varies with the method of conversion, the raw material, and the humidity of the atmosphere. Schwalbe found 1.2 to 6.3 per cent; Ost and Westoff,[4] 4.30 to 4.75 per cent. Absolutely dry hydrocelluloses prepared from sulphite cellulose, after standing under a bell jar in an atmosphere saturated with moisture, contained 9.24 to 11.87 per cent of water.[5] Knoevenagel[6] found 8.8 to 9.6 per cent hygroscopic moisture for his product in comparison with 4.15 per cent for a hydrocellulose prepared by Girard's method.

Effect of Heat.—Girard found that his hydrocellulose when heated in the presence of air turned yellow even at 50°; at 100° the decomposition was rapid. The colored product formed could be removed by washing with water. His hydrocellulose evidently contained traces of acid, since properly purified products are usually stable at 125 to 130°.[1] Bay[2] states that the pure product is stable even at 180°.

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[1] E. Knoevenagel, *l.c.*

[2] F. Heuser and F. Eisenring, *Cellulosechemie*, **4** (1923), 25.

[3] C. F. Cross and E. J. Bevan, *Chem. Ztg.*, **33** (1909), 368.

[4] H. Ost and F. Westhoff, *Chem. Ztg.*, **33** (1909), 197.

[5] W. Qvist, *l.c.*

[6] E. Knoevenagel, *l.c.*

Action of Acids and Alkalis.—It has been claimed for hydrocellulose that it is very resistant towards acids and alkalis. A product, highly resistant to these reagents, is obtained by treating cellulose with hydrochloric acid at a temperature of 60 to 70°, in the presence of a quantity of potassium chlorate insufficient to convert the cellulose to oxycellulose.[3] Boiling dilute acid had little effect on the hydrocelluloses prepared by Büttner and Neumann,[4] while boiling with caustic alkali produced only a yellow coloration.

Hydrocelluloses prepared by various methods usually show a high solubility in alkali. Girard's hydrocellulose, prepared with hydrochloric acid gas, when boiled with 10 parts of 10 per cent sodium hydroxide, showed increased solubility with the length of heating; 85 per cent remained undissolved after 5 minutes and 55 per cent after 30 minutes.[5] Schwalbe[6] found that Girard's hydrocellulose had the following solubilities in boiling 15 per cent sodium hydroxide:

Hydrocellulose, grams	NaOH solution, grams	Time of boiling, minutes	Undissolved residue, per cent
10	200	10	48
10	200	20	42
10	200	30	40
10	200	40	37
10	400	60	33

Strong caustic soda dissolves about one-third of hydrocellulose, the residue being mercerized and its copper number greatly reduced. Of the dissolved portion, about 85 per cent can be reprecipitated with acids.[7] The hydrocelluloses prepared by

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[1] H. Ost, *Z. angew. Chem.*, **19** (1906), 994; *Ann.*, **398** (1913), 313.

[2] C. Bay, Diss. Giessen (1913), p. 33.

[3] "Fabrik Chemischer Preparate von R. Sthamer," G. P. 123122 (1900).

[4] G. Büttner and J. Neumann, *Z. angew. Chem.*, **21** (1908) 2609.

[5] C. G. Schwalbe, *Z. angew., Chem.*, **20** (1907), 2171.

[6] C. G. Schwalbe, *Z. angew. Chem.*, **22** (1909), 156.

[7] H. Jentgen, *Z. angew. Chem.*, **23** (1910), 1545.

Qvist[1] were soluble to the extent of 41.4 to 66.5 per cent in 10 per cent caustic soda. Bay[2] found solubilities of 54.94 to 58.80 per cent, after heating for 2 hours with 10 per cent caustic soda. On the other hand, Knoevenagel's hydrocellulose is completely soluble in 8 per cent caustic soda in the cold.

Hydrocellulose, on heating with lime water, gave the same or similar products as did oxycellulose, namely, isosaccharinic acid and an amorphous salt of what was apparently dihydroxybutyric acid.[3] Hydrocellulose, as usually prepared, behaves as a mixture of cellulose and hydrocellulose, the latter being removable by heating with solutions of the alkaline earths.[4] Girard's hydrocellulose on boiling with lime showed a loss in weight of 11.6 per cent in 30 minutes, and 24.4 per cent in 12 hours.[5]

Hydrocellulose, when heated with alkali under pressure, gave large yields of acetic acid.[6] With potassium carbonate solution at 100 to 110°, 14 per cent of acetic acid was obtained. Potassium hydroxide at 150° gave 19.5 per cent of acetic acid, while heating for 8 hours in a closed vessel gave 41.7 per cent.

A hydrocellulose prepared by Vignon[7] gave 9.7 per cent of glucose when 2 grams were heated on the water bath for 6 hours with 50 cubic centimeters of hydrochloric acid (sp. gr. 1.125) and 200 cubic centimeters of water. Its heat of combustion was 4006 calories. Hydrocelluloses prepared by boiling cellulose with hydrochloric acid, with and without stannous chloride, were capable of giving the same amount of furfural, namely, 0.86 per cent.[8]

Schwalbe[9] found that Girard's hydrocellulose was more resistant to hydrolysis with 5 per cent sulphuric acid than cotton. The copper number due solely to hydrolysis (hydrolysis difference) was 0.9 for hydrocellulose. Bay[1] found hydrolysis differences of 3.69 to 5.25.

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[1] W. Qvist, *l.c.*

[2] C. Bay, *l.c.*

[3] J. J. Murumow, J. Sack, and B. Tollens, *Ber.*, **34** (1901), 1431.

[4] C. G. Schwalbe and E. Becker, *J. prakt. Chem.*, **100** (1919), 19.

[5] H. Ost and R. Bretschneider, *Z. angew. Chem.*, **34** (1921), 422.

[6] C. F. Cross and E. J. Bevan, *J. Soc. Chem. Ind.*, **11** (1892), 966–969.

[7] L. Vignon, *Compt. rend.*, **131** (1900), 708.

[8] L. Vignon, *Compt. rend.*, **126** (1898), 1355.

[9] C. G. Schwalbe, *Z. angew. Chem.*, **22** (1909), 201.

Certain forms of hydrocellulose appear to be very resistant to further hydrolysis with dilute acids under pressure or with concentrated acids in the cold. This difference has been attributed to the formation of reversion products by the interaction of reducing sugars with the residue in the colloidal phase; hence the so-called hydrocellulose remaining after the prolonged heating of cellulose with dilute acids is not in the strict sense an intermediate degradation product.[2] Koerner[3] found that hydrocellulose gave a much higher yield of dextrose, as determined by fermentation to alcohol, than did sulphite cellulose when heated with dilute acid under pressure; the yields of alcohol were 17.95 and 12.83 per cent respectively. Krull[4] subjected Girard's hydrocellulose to hydrolysis with strong hydrochloric acid and obtained only 13.2 per cent of sugar; the residue amounted to 77.28 per cent. A preliminary treatment with chlorine increased the yield of sugar to 69.6 per cent. On the other hand, Knoevenagel's hydrocellulose gave over 95 per cent of fermentable glucose when hydrolyzed with 41 per cent hydrochloric acid.[5]

Solubility.—Hydrocellulose dissolves easily in all the known cellulose solvents. Girard[6] found that it dissolved instantly in Schweizer's reagent. Some confusion has originated on this point. The statement of Bronnert[7] that it dissolved only slightly in Wright's solution has been interpreted[8] as referring to Schweizer's reagent. In concentrated cuprammonium solution, hydrocellulose forms 10 to 15 per cent solutions.[9] The cuprammonium solutions show remarkably low viscosities.[10]

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[1] C. Bay, *l.c.*, p. 32.

[2] A. Wohl and K. Blumrich, *Z. angew. Chem.*, **34** (1921), 17–18.

[3] T. Koerner, *Z. angew. Chem.*, **21** (1908), 2357.

[4] H. Krull, Diss. Danzig (1916), p. 42.

[5] E. Heuser and F. Eisenring, *Cellulosechemie*, **4** (1923), 25.

[6] A. Girard, *Ann. chim. phys.*, [5] **24** (1881), 364.

[7] E. Bronnert, G. P. 109996 (1899).

[8] C. G. Schwalbe, *Z. angew. Chem.*, **20** (1907), 2171.

[9] H. Jentgen, *Z. angew. Chem.*, **23** (1910), 1546.

[10] H. Ost, *Z. angew. Chem.*, **24** (1911), 1896.

Action of Dyes.—Girard[1] noted that hydrocellulose had a greater affinity for dyes than ordinary cotton. According to Witz,[2] it is not dyed by basic dyestuffs. Schwalbe[3] found that ponceau 2R, brilliant crocein M, and patent blue, dyed hydrocellulose, prepared by Girard's method with 3 per cent sulphuric acid, more strongly than cotton. With mikado orange there was no difference, while with benzopurpurine 10B, hydrocellulose was dyed more weakly than cotton. Hydrocellulose and its nitrate took up more methylene blue than cotton cellulose and its nitrate.[4]

Harrison[5] performed a series of experiments in which dilute sulphuric acid was allowed to dry on cotton, and found that the resulting products took up more methylene blue and less direct dyestuffs than cotton, properties usually attributed to oxycellulose. He concluded that the acid treatment probably formed colloidal hydrocellulose.

The various discrepancies, with respect to the affinity of hydrocellulose for dyestuffs, are without doubt due to the lack of uniformity of the hydrocelluloses prepared by various authors. Not only the amount of actual hydrocellulose, but the presence of gelatinized cellulose, some oxycellulose, and the fixation of a portion of the acid, particularly sulphuric acid, used in converting the cellulose to hydrocellulose, must be considered.

When cotton fabrics are subjected successively to printing with a strong solution of oxalic acid thickened with dextrin, air drying, and washing, the printed parts, while not tendered, show a decreased affinity for direct dyes and a marked affinity for methylene blue.[6] Boiling with dilute sodium hydroxide destroys this property. Cellulose appears to be capable of combining with small amounts of oxalic, malonic, and hexylmalonic acids, but not with tartaric, citric, succinic, and glutaric acids. It has been further shown[1] that when hydrocellulose is prepared by treating cellulose with dilute sulphuric acid (5 to 10 per cent) and drying at low temperatures (40 to 50°), the cellulose fixes 0.97 to 1.14 per cent of sulphuric acid, which acts as a mordant for basic dyes.

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[1] A. Girard, *l.c.*, p. 369.

[2] G. Witz, *Bull. Rouen*, **11** (1883), 220.

[3] C. G. Schwalbe, "Chemie der Cellulose" (1911), p. 219.

[4] E. Berl and R. Klaye, *Z. Schiess-u. Sprengstoff.*, **2** (1907), 381.

[5] W. Harrison, *J. Soc. Dyers Colourists*, **28** (1912), 238–239; *cf.* E. Grandmougin, *Z. Farben-Ind.*, **3** (1907), 6.

[6] E. Knecht, *Seventh Int. Cong. Appl. Chem. London*, Sec. IVA (1909), 51.

Hydrocellulose Nitrate.—Hydrocellulose nitrate contains as much nitrogen as cellulose nitrate, but it is more rapidly attacked by potassium hydroxide. It reduces Fehling's solution and shows slight aldehyde properties with Schiff's reagent.[2] The acetone solutions of hydrocellulose nitrate show a very low viscosity.[3]

The nitrogen content of a nitrated hydrocellulose was 13.25 per cent in comparison with 13.5 per cent for the corresponding derivative from cotton. Hydrocelluloses prepared from sulphite cellulose and cotton, by the action of nitric acid of sp. gr. 1.1 (17.1 per cent) in the cold for about 1 year, when nitrated in the cold with nitric acid of sp. gr. 1.4 to 1.5, gave xyloidins having a nitrogen content almost identical with that of the xyloidins prepared from cotton.[4]

Formula.—Girard gave hydrocellulose the formula $(C_6H_{10}O_5)_2.H_2O$. Stern[5] erroneously denied the formation of hydrocellulose by the action of dilute acids. He obtained for the treated cellulose analyses agreeing closely with $C_6H_{10}O_5$, and concluded that Girard's hydrocellulose must have contained free acid and water. Büttner and Neumann[6] obtained for hydrocellulose dried at 100° the general formula $(C_6H_{10}O_5)_x.H_2O$, in which x is 2, 3, and 6, depending on the method used for its preparation. Ost[7] arrived at the formula $(C_6H_{10}O_5)_6.H_2O$ for material dried at 120°, but later,[8] after a careful series of analyses, came to the conclusion that hydrocellulose dried at 120° could not be distinguished in elementary composition from ordinary cellulose.

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[1] E. Knecht and F. P. Thompson, *J. Soc. Dyers Colourists*, **37** (1921), 270–272.

[2] L. Vignon, *Compt. rend.*, **126** (1898), 1658.

[3] E. Berl and R. Klaye, *Z. Schiess-u. Sprengstoff.*, **2** (1907), 381.

[4] C. Haeussermann, *Z. angew. Chem.*, **26** (1913), 456.

[5] A. L. Stern, *J. Chem. Soc.*, **85** (1904), 336–340.

[6] G. Büttner and J. Neumann, *Z. angew. Chem.*, **21** (1908), 2609; **22** (1909), 585.

[7] H. Ost, *Z. angew., Chem.* **19** (1906), 994; H. Ost and F. Westhoff, *Chem. Ztg.*, **33** (1909), 198.

[8] H. Ost, *Ann.*, **398** (1913), 319.

Nature of Hydrocellulose.—The nature and the composition of hydrocellulose have been the subject of considerable speculation. Jentgen[1] thought that hydrocellulose prepared with sulphuric acid of sp. gr. 1.453 to 1.530 was a mixture of hydrocellulose and oxycellulose together with unchanged cellulose.

Hauser and Herzfeld[2] see in hydrocellulose an adsorption compound of variable composition, consisting of cellulose with its hydrolytic products, such as dextrins and dextrose. The property of brittleness is due to the presence of gelatinized cellulose, or its gelatinized degradation products, which are brittle in the dry state. Girard's hydrocellulose was extracted with water in a Soxhlet extractor and the cupric reducing power of the residue was determined at intervals of 12 hours. The original copper number of 5.4 decreased rapidly during the first hours of extraction, dropping to 0.8 after 93 hours. When the residue was again treated by Girard's method, the copper number of 4.0 decreased to 0.8 after 71 hours' additional extraction. Judging from the extraction curve, the hydrocellulose behaved as a gel containing adsorbed degradation products of cellulose. Glucose was identified in the aqueous extract. Harrison[3] had previously advanced the opinion that hydrocellulose consisted of the hydrolytic products of cellulose adsorbed by peptized cellulose.

By boiling hydrocellulose with Fehling's solution, a residue of pure cellulose is obtained after treatment with acid to remove the cuprous oxide, and washing with water.[4] The residue from the treatment of hydrocellulose with alkalis shows a considerable difference from ordinary cellulose. Ost and Bretschneider[5] found that the viscosities of cuprammonium solutions of hydrocellulose and the residue from boiling the latter with lime water were practically identical. The viscosity of a solution of a nitrating cotton that had been boiled with lime water decreased after standing 7 days to the value for hydrocellulose. Acetylation of the hydrocelluloses and residues, as well as of the nitrating cotton and residue, and the determination of the percentage of the acetylated product soluble in acetone, showed that the solubilities of the hydrocelluloses and their residues were practically identical. The conclusion is drawn that the residue is essentially the same as the original hydrocellulose, differing therefrom only in a lower copper number.

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[1] H. Jentgen, *Z. angew. Chem.*, **23** (1910), 1545.

[2] O. Hauser and H. Herzfeld, *Chem. Ztg.*, **39** (1915), 689–690; *cf.* C. G. Schwalbe and E. Becker, *J. prakt. Chem.*, **100** (1919), 19.

[3] W. Harrison, *J. Soc. Dyers Colourists*, **28** (1912), 359.

[4] W. Netthofel, "Beiträge zur Kenntnis der Zellulose," Diss. Berlin (1914), p. 28.

[5] H. Ost and R. Bretschneider, *Z. angew. Chem.*, **34** (1921), 422–423.

According to Heuser,[1] true hydrocellulose consists of a dimeric anhydrocellobiose molecule in which an active carbonyl group is formed at the expense of an anhydride position, but without depolymerization of the dimeric molecule. The cellulose recovered from cellulose acetate has long been recognized as hydrocellulose. Barnett[2] has obtained what he considers definite hydrazones of the cellulose acetates with phenylhydrazine and *p*-bromphenylhydrazine.

Amyloid and Parchment.—It was observed by Schleiden[3] that when plant fibers were treated for half a minute with a mixture of three parts of concentrated sulphuric acid and one part of water, then iodine added, they were colored blue. The supposed transformation into starch was refuted by Liebig,[4] who showed that if the gelatinous cellulose obtained by Schleiden's method was washed after the acid treatment, tincture of iodine did not give a blue color. When the acid was filtered rapidly from the cellulose, and iodine solution added to the clear filtrate, a dark-blue precipitate was obtained. Water added to the filtrate precipitated a white flocculent substance that gave the blue color with iodine.

The interesting discovery was made by Poumarède and Figuier[5] that, when filter paper was dipped into sulphuric acid of 66° Bé. (93.5 per cent) for half a minute and then into dilute ammonia to arrest the reaction, the paper resembled animal parchment. It was called "papyrine." Similar products were later known as vegetable parchment and amyloid.

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[1] E. Heuser and W. von Neuenstein, *Cellulosechemie*, **3** (1922), 89.

[2] W. L. Barnett, *J. Soc. Chem. Ind.*, **40** (1921), 61–63T.

[3] M. J. Schleiden, *Ann.*, **42** (1842), 302.

[4] J. Liebig, *Ann.*, **42** (1842), 306–309.

[5] J. A. Poumarède and L. Figuier, *Compt. rend.*, **23** (1846), 918.

Strong sulphuric acid produces various products. Béchamp[1] found that the dissolved cellulose could be precipitated with water and obtained in two water-soluble forms, "wood dextrin," and a gelatinous mass soluble in cold water. The latter product is very similar to the soluble cellulose of Guignet.[2] Hoffmann[3] thought that the paper underwent no chemical change by being parchmentized.

Paper can be parchmentized with nitric acid and various salts. Filter paper is remarkably toughened by moistening with nitric acid of sp. gr. 1.42 and subsequently washing with water. The strength is increased tenfold. The paper contains no nitrogen.[4] Rankin[5] states that paper so treated is nitrated to some extent. During drying there is a linear shrinkage of about 10 per cent.

Ferwer[6] treated 1 part of cotton with 30 parts of a mixture of 4 parts of concentrated sulphuric acid and 1 part of water in a mortar; in half a minute he obtained a stiff jelly which in 15 minutes gradually liquefied. Water precipitated a structureless, gelatinous mass, amyloid, which was colored blue by iodine, but the color disappeared on washing with water. The mass swelled in water to a paste which dried to thin, transparent films when spread upon glass. The acid solution gave dextrins and sugar on long standing.

Guignet[7] obtained a cellulose forming a colloidal solution with water by treating filter paper or cotton with sulphuric acid of 50° Bé. (62.5 per cent). The transparent, gelatinous mass did not change in the presence of an excess of acid at ordinary temperature but at about 100° dextrins were formed rapidly. The acid was removed by washing with water, finally with absolute alcohol. The washed product, dried at a low temperature to remove the alcohol, gave a milky solution on digestion with water. The solution was difficult to filter, did not settle out on standing, and remained colloidal when heated. The solution was slightly dextro-rotatory but did not reduce Fehling's solution. The semitransparent films, obtained by drying the solution on marble coated with vaseline, passed into colloidal solution again when treated with water. The films became insoluble in water when plunged into sulphuric acid of 55 to 60° Bé.

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[1] A. Béchamp, *Compt. rend.*, **42** (1856), 1213.

[2] C. E. Guignet, *Compt. rend.*, **108** (1889), 1258–1259.

[3] A. W. Hoffmann, *Ann.*, **112** (1859), 243.

[4] E. Francis, *J. Chem. Soc.*, **47** (1885), 183–185; C. Beadle, *Chem. News*, **112** (1915), 143–144.

[5] W. R. Rankin, *Pharm. J.*, **95** (1915), 36.

[6] J. Ferwer, *Dinglers polytech. J.*, **159** (1861), 218–221.

[7] C. E. Guignet, *l.c.*

Parchment paper consists of ordinary cellulose coated with colloidal cellulose (hydrocellulose). Guignet explained the disintegrating action of hot water on thin parchment paper to removal of colloidal cellulose. Thicker paper is not so affected, owing to the use in its manufacture of a stronger acid than that producing soluble cellulose.

While studying the saccharification of cellulose, Flechsig[1] obtained an amyloid by dissolving cotton in 69 per cent sulphuric acid. The cotton (250 grams) was treated with a cold mixture of 250 grams of sulphuric acid (75 per cent SO_3) and 84 grams of water. After standing an hour, addition of water gave a precipitate of amyloid which was held to be an intermediate product in the transformation of cellulose into dextrin.

Zemplén[2] obtained only 15 to 20 per cent of octacetylcellobiose from Flechsig's amyloid, in comparison with 50 to 55 per cent obtained by Klein[3] from hydrocellulose and cellulose. The conclusion was drawn that amyloid and hydrocellulose are not identical.

When wood is dissolved in strong sulphuric acid (78 to 93 per cent) at 10 to 40°, it is converted into "acid cellulose" which can be thrown down by dilution with water. According to Ekström,[4] the product has a pronounced acid character but not that of an aldehyde. Complete conversion to glucose is obtained by heating with sulphuric acid at pressures slightly above atmospheric. Acid cellulose is insoluble in water, but forms water-soluble sodium salts. Schulz,[5] working with cotton and 78 per cent sulphuric acid, was unable to confirm these results. Acid cellulose had no pronounced acid character and contained aldehyde groups, as shown by the high copper number of 11.2.

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[1] E. Flechsig, *Z. physiol. Chem.*, **7** (1883), 523–540.

[2] G. Zemplén, *Z. physiol. Chem.*, **85** (1913), 180–192.

[3] F. Klein, *Z. angew. Chem.*, **25** (1912), 1409.

[4] G. Ekström, G. P. 193112 (1907); 207354 (1909).

[5] W. Schulz, "Zur Kenntnis der Cellulosearten," Berlin (1911), 100 pp.

Cotton fabric immersed in 62.5 per cent sulphuric acid at 0° for 10 minutes, and washed, forms a transparent leathery product.[1] It takes up water very easily and is dyed much more intensely in an indigo bath than the ordinary fabric.

A thorough investigation of the initial degradation products of cellulose by strong sulphuric acid was made by Schwalbe and Schulz.[2] Sulphuric acid of a concentration of 62.5 per cent gives Guignet's soluble cellulose, 69 per cent, "amyloid," and 78 per cent, parchment, which is not identical with amyloid. Acids of higher concentration rapidly produce sulpholysis with the formation of acid esters.

Guignet's Soluble Cellulose.—Five grams of air-dry cotton and 85 cubic centimeters of 62.5 per cent sulphuric acid are triturated in a mortar for 15 minutes. The mass is allowed to stand at room temperature with frequent stirring for 5 hours, 170 cubic centimeters of water added, intimately mixed, and filtered on a cloth filter; the portion in colloidal solution in the filtrate is disregarded. The residue is washed free from acid by decantation, a procedure frequently requiring several days.

Flechsig's Amyloid.—Five grams of absorbent cotton are gradually introduced into 40 grams of 69 per cent sulphuric acid during a period of 1 to 2 hours. The temperature, initially 6 to 19°, is held below 30° by cooling. The mass becomes viscous, syrupy, then grayish white and opaque. Water precipitates a white flocculent mass, a large part of which passes into milky colloidal solution when suctioned on a cloth filter. The residue is washed free from acid by decantation.

Parchment.—The cellulose is immersed in 78 per cent sulphuric acid for a few seconds, the time depending on the physical character of the cellulose. Filter paper is treated for 20 seconds and loose cotton for 10 seconds, then washed free from acid. The fibers become soft and transparent. The swelling of the fibers is usually followed by shrinkage. A portion of the cellulose passes into colloidal solution during the acid treatment, the solubility increasing with prolongation of the treatment.

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[1] W. Minajeff, *Z. Farben-Ind.*, **9** (1910), 65.

[2] C. G. Schwalbe and W. Schulz, *Ber.*, **43** (1910), 913–917; *Z. angew. Chem.*, 26 (1913) 499–501; W. Schulz, *l.c.*

Some of the properties of these modified celluloses are given in the following table:

Material	Copper number corrected	Hydrolysis number corrected	Difference due to hydrolysis	Water (dried at 105°), per cent	Solubility in 10 per cent NaOH, per cent
Absorbent cotton	0.20	2.7	2.5	5.2	8.6
Filter paper	1.95	4.45	2.5	5.5	20.4
Soluble Guignet cellulose	10.76	7.26	−3.5	2.4	70.1
Parchmentized Guignet cellulose	18.8	20.5	1.7	4.5	73.3
Typical Flechsig amyloid	18.36	26.67	8.3	12.0*	99.4
True parchment from:					
Absorbent cotton	7.11	17.63	10.5	9.3	70.1
Filter paper	4.9	15.7	10.8	9.0	18.3
Ekström acid cellulose	11.2	30.4	19.2	7.0*	100.0

* At 95°.

Guignet's soluble cellulose and Flechsig's amyloid, like ordinary cotton, are not stained blue by iodine-potassium iodide solution, except in the presence of sulphuric acid; parchment paper, the closely related parchmentized Guignet cellulose, and Ekström's acid cellulose are all stained blue. With respect to colloidal properties, Guignet's cellulose stands first as a typical reversible hydrogel, followed by Flechsig's amyloid, and Ekström's acid cellulose.

The maximum permissible drying temperature for Flechsig's amyloid and Ekström's acid cellulose is only 95°; the remaining modified celluloses may be dried at 105° without producing decomposition.

As to solubility in alkali, Flechsig's amyloid and Ekström's acid cellulose are about equal, while decreasing solubility is shown by Guignet's cellulose, parchmentized Guignet cellulose, parchment paper, and cotton in their order. Flechsig's amyloid is most hygroscopic and Guignet's cellulose least so.

With reference to hydrolysis differences, Guignet's cellulose with a negative difference (−3.5) is evidently a product inclined to reversion. Parchmentized Guignet cellulose is not, as Guignet assumes, a true parchment, as shown by the hydrolysis difference, 1.7 in place of 10.7. On the other hand, Flechsig's amyloid with 8.3 approaches closely to true parchment, which supports the assumption that parchment is a mixture of cellulose, amyloid, and hydrocellulose.

Cellulose Dextrins and Sulphuric Esters.—In 1819, Braconnot[1] found that when linen was left in contact with sulphuric acid (sp. gr. 1.827) at room temperature for some time, the solution neutralized with lime, filtered, and the filtrate evaporated to dryness, there was obtained a gummy mass, which he called "acide-végéto-sulfurique." The latter on hydrolysis was convertible into glucose. Blondeau de Carolles,[2] on studying the reaction, found that cellulose sulphuric esters of different composition were obtainable according to the time in which the acid and the cellulose were in contact. The following water-soluble barium salts were isolated:

Reaction period, hours	Composition of the salts
0.5	$C_{18}H_{36}O_{18}(SO_3)_2BaO.2H_2O$
12	$C_{10}H_{20}O_{10}(SO_3)_2BaO.2H_2O$
24	$C_4H_8O_4(SO_3)_2BaO.2H_2O$

It was established that the ratio of BaO to SO_3 was constantly 1:2, a relationship confirmed by subsequent investigators. Fehling,[3] using linen, obtained a salt with the following composition:

	Per Cent
BaO	5.0
SO_3	5.3
C	35.8
H	5.9

This corresponds with the formula $C_{90}H_{180}O_{90}(SO_3)_2.BaO$. Marchand,[4] after leaving Swedish filter paper in contact with sulphuric acid for some weeks, isolated a "wood sulphuric acid" of the composition $C_{33}H_{28}O_8(SO_3)_2.CaO$. It was observed by Béchamp[5] that the products obtained with concentrated sulphuric or hydrochloric acid resembled starch dextrin but had a lower rotatory power. He called one of the soluble products "wood dextrin," an unfortunate term that still persists.

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[1] H. Braconnot, *Ann. chim. phys.*, [2] **12** (1819), 172.

[2] Blondeau de Carolles, *Ann.*, **52** (1844), 412.

[3] H. Fehling, *Ann.*, **53** (1845), 134–136.

[4] Marchand, *J. prakt. Chem.*, **35** (1845), 199–201.

[5] A. Béchamp, *Ann.*, **100** (1856), 366–367.

Hönig and Schubert[1] dissolved 10 grams of cotton in 40 cubic centimeters of concentrated sulphuric acid and studied the effect of time and temperature. Time had relatively little effect on the composition of the barium salts, but the optical activity rose decidedly with the temperature, as can be seen from the following data:

Temperature	Ba, per cent	Rotation, $[\alpha]j$
+7°	25.37	− 3.65°
10	26.65	− 1.62
20	26.75	+37.05
25	24.34	+44.10
33	25.40	+57.36
40	25.29	+72.99

The composition of the salts and their optical activity were not affected unless the ratio of acid to cellulose fell below 2:1. The barium content increased slightly and the optical activity considerably with the time of reaction. A cellulose solution showed the following changes:

	Ba, per cent	$[\alpha]j$
After 0.5 hour..........................	24.34	+44.10°
After 24 hours..........................	25.71	+67.77

The barium salts were easily soluble in water and insoluble in alcohol; they reduced Fehling's solution and formed white to yellow, apparently crystalline powders. The free acids were very hygroscopic, amorphous substances which on boiling with alcohol decomposed into sulphuric acid and cellulose dextrins. General formulæ are given for the acid esters and salts, but these must be accepted with reservation, since ultimate analyses were not made.

Acid esters: $C_{6n}H_{10n}O_{5n-x}(SO_4)_x$.

Salts: $C_{6n}H_{10n}O_{5n-x}(SO_4M')_x$.

When one part of cellulose and two parts of sulphuric acid were allowed to stand 30 minutes, diluted with ten parts of absolute alcohol and let stand 24 hours, acid esters were deposited; on boiling the latter with water, a series of compounds were obtained from amyloid to dextrins, according to the temperature.[1] On increasing the reaction temperature from 3 to 40°, the optical rotation of the resulting products increased from $[\alpha]_j = +6.4°$ to $+127.72°$; the solubility in water increased and the coloration with iodine passed from blue through bluish violet, violet, and red to colorless. The color reactions greatly resembled those obtainable with the degradation products of starch.

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[1] M. Hönig and S. Schubert, *Monatsh.*, **6** (1885), 708–728.

Stern[2] dissolved cotton in sulphuric acid, and after a total reaction period of 7 hours, he prepared the barium salt of cellulose disulphuric acid, $C_6H_8O_5(SO_3)_2Ba$. The free acid obtained by removing the barium with sulphuric acid was very unstable and difficult to isolate. Hydrolysis of the barium salt with 2 per cent sulphuric acid for 30 minutes gave glucose and a product corresponding with $C_{18}H_{28}O_{15}.(SO_3H)_2$; longer hydrolysis led to glucose and compounds with a diminishing content of sulphuric acid. The first product of hydrolysis was the ester, $C_6H_9O_5.\text{-}SO_3H$, which, like the parent substance, had no action on Fehling's solution.

Cellulose dextrins were prepared by Yllner[3] by dissolving Swedish filter paper in 80 per cent sulphuric acid, and after 12 hours, neutralizing with chalk. The glucose was removed by fermentation with yeast. The free dextrins were obtained by boiling the calcium salts with alcohol and fractionally precipitating them from aqueous solution with alcohol. Contrary to the findings of Hönig and Schubert[4] the cupric reducing power of the dextrins increased with the increase in rotatory power. The highest rotation observed for any of the dextrins was $[\alpha]_D = +107.5°$.

The influence of time, temperature, amount and concentration of acid, on the formation of dextrin esters was studied by Mühlmeister.[5] The effect of time is shown in the table below.

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[1] M. Hönig and S. Schubert, *Monatsh.*, **7** (1886), 455–468.

[2] A. L. Stern, *J. Chem. Soc.*, **67** (1895), 74–90.

[3] C. A. Yllner, *Z. angew. Chem.*, **25** (1912), 103–107.

[4] M. Hönig and S. Schubert, *l.c.*, 463.

[5] H. Mühlmeister, "Beiträge zur Hydrolyse und Sulfolyse der Zellulose," Diss. Hannover (1913), 44 pp.

The cellulose was dissolved in 70 per cent sulphuric acid at 15° and the esters precipitated with alcohol-ether mixture. With time the yield of esters decreased, while the sulphuric acid content and reducing power of the esters and dextrins remaining in solution in the alcohol-ether mixture, increased. When 75 cubic centimeters of 70 per cent sulphuric acid were allowed to act on 2 grams of cotton for 6 hours, the solution diluted with an equal volume of water and let stand 24 hours, the esters, on precipitation, had a sulphuric acid content of 26.2 per cent, which corresponds with $C_{12}H_{19}O_{10}.SO_3H$.

INFLUENCE OF TIME ON THE PROPERTIES OF DEXTRIN ESTERS

Hours	Yield from 1.887 grams cellulose	Corrected copper number	Sulphuric acid, per cent	Milligrams reduced copper from 25 cubic centimeters of solution	Solubility in water
1	1.847	12.4	6.6	....	−
2	1.761	19.7	8.1	....	−
3	1.651	24.6	9.6	1.7	+
4	1.566	22.4	11.7	3.6	+
5	1.410	25.9	11.4	5.6	+
6	1.274	25.9	12.8	6.8	+
7	1.477	25.2	10.5	3.9	+
8	1.322	27.8	11.0	5.7	+
9	1.074	27.5	11.0	7.7	+
10	.....	....	....	9.2	+
11	0.534	34.3	12.1	....	+
12	.....	....	....	11.4	+

Thirty grams of cotton were allowed to react with 300 cubic centimeters of 70 per cent sulphuric acid for 20 hours. Addition of 2 liters of alcohol precipitated 3.1 grams of an ester having a copper number of 37.8 and a rotation in aqueous solution of $[\alpha]_D^{20°} = +15.4°$. The ester, though originally soluble in water, was rendered partially insoluble by boiling with alcohol. There was obtained 40 per cent of water-soluble dextrin and 60 per cent of water-insoluble dextrin; the copper numbers were 57.9 and

43.9 respectively. Ether precipitated from the alcoholic solution two esters having the following properties:

	Copper number	$[\alpha]_D^{20°}$	H_2SO_4 content
1	33.4	+21.1°	
2	118.9	+54.3	18.9

The cellulose dextrins, on acetylation, gave products containing 63 to 72 per cent of acetic acid. The acetates soluble in ether corresponded with glucose pentacetate and glucose tetracetate. Cellobiose octacetate could not be detected.

Ost[1] is of the opinion that Hönig and Schubert did not obtain true dextrins but rather condensation products resulting from reversion of the dextrins by the concentrated sulphuric acid. Concentrated sulphuric acid forms dextrin esters, but for the sulpholysis of cellulose, 70 per cent sulphuric acid is a better reagent. Acid of a concentration of 56 per cent does not form esters with cellulose in the cold.[2]

Esparto cellulose, containing about 20 per cent of pentosans, gave on sulpholysis esters in which Ba was approximately equal to SO_4, the ratio being $Ba_2:(SO_4)_3$. This indicates that some of the barium must be combined with hydroxyl groups of a sufficiently acid character to decompose barium carbonate.[3] The stable character of the sulphate residues is indicated by the fact that their elimination was complete only after boiling with concentrated hydrochloric acid, in the presence of barium chloride, for some hours. On treating 60 grams of esparto cellulose with 300 cubic centimeters of 73 per cent sulphuric acid for 24 hours, diluting with water, and fractionally precipitating with alcohol, two fractions were obtained as follows:

Number	Yield, grams	Ba, per cent	SO_4, per cent	Furfural, per cent	$[\alpha]_D$
A	37	8.6	7.9	8.3	+47.8 to 45.5°
B	8	8.6	10.6	8.0	+55.3 to 51.6°

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[1] H. Ost, *Ann.*, **398** (1913), 322.

[2] E. Flechsig, *Z. physiol. Chem.*, **7** (1883), 528.

[3] M. Cunningham, *J. Chem. Soc.*, **113** (1918), 173–181.

Cotton cellulose was hydrolyzed with 40 per cent hydrochloric acid for 48 hours. The following lead salts were isolated:

Number	Pb, per cent	Cl, per cent	$[\alpha]_D$
A	8.3	6.2	+42.5 to 34.5°
B	9.4	9.8	+26.7 to 17.3°

It is interesting to note that the above salts contain chlorine, and that esparto cellulose when hydrolyzed under similar conditions gave very similar esters containing chlorine.

An extensive investigation of cellulose dextrins has been made by Samec and Matula.[1] The raw material was sulphite cellulose. The authors used sulphuric acid (50 to 85 per cent) and phosphoric acid (76 to 85 per cent) at temperatures of 50 to 70° for variable periods up to 6 days. The course of the reaction was followed by: (1) the reaction with iodine, the color changing from blue through violet to brown; (2) the change in the proportion of the products soluble in water; (3) the effect of alcohol in which

a. The dextrin esters gelatinize and the dextrin precipitates.
b. The dextrin esters and dextrins are insoluble.
c. The dextrin esters are soluble but the dextrins insoluble.
d. Both dextrin esters and dextrins are soluble.

Five different dextrins were prepared as follows:

A. By the action of 50 parts of 55 per cent sulphuric acid on 2 parts of cellulose at 20° for 45 minutes.

B. In the same way as A, except that the reaction was prolonged until water caused no separation, *i.e.*, 4 to 5 hours.

C. By the action of 5 parts of 55 per cent sulphuric acid on 2 parts of cellulose for 24 hours.

D. By the action of 20 parts of 85 per cent phosphoric acid on 1 part of cellulose for 1 hour at 50°.

E. By the action of 25 parts of 80 per cent phosphoric acid on 1 part of cellulose for 24 hours at 50°.

The reaction products were dialyzed until free from electrolytes, a process requiring weeks. Some of the properties of these dextrins are given below. Judging from titration with sodium hydroxide, one $-SO_4H$ group is combined with 41 to 42 $C_6H_{10}O_5$ groups in dextrin A, and with six $C_6H_{10}O_5$ groups in dextrin C.

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[1] M. Samec and J. Matula, *Kolloidchem. Beihefte*, **11** (1919), 37–73.

Dextrin	Solubility		Iodine reaction*	Copper number	Dialyzable portion, per cent	Molecular weight of non-dialyzable residue
	In water	In alcohol				
A	Slight	Gelatinous	Blue	15.8	7	6800
B	Soluble	Insoluble	Bluish violet	36.9	75	2400
C	Soluble	Insoluble	Bluish violet	49.8	50	6400
D	Slight	Gelatinous	Blue	8.6	..	15000
E	Soluble	Soluble	Dark violet	....	70	3000–4000

* With the sulphuric acid solutions.

The action of diastase on the dextrins was also studied. Dextrin A in the form of a suspension was not noticeably attacked; after 2 hours' action on the colloidal solution, the copper number was reduced from 15.8 to 6.9, at which point the dextrin became flocculent. Dextrin B resembled starch in that the viscosity decreased, the reducing power increased, and a fermentable sugar was formed after 2 hours. Dextrin C resembled B, while D was not attacked. Dextrin E differed only quantitatively from the dextrins prepared with sulphuric acid.

When benzene or its homologs is added to a solution of cellulose in strong sulphuric acid, a reaction takes place to give an amorphous, infusible compound, insoluble in the ordinary solvents; these are called desoxyns.[1] The phenyl group is evidently directly connected with a carbon atom in the carbohydrate, since phenyldesoxyn, $C_6H_7O_2.(C_6H_5)_3$, gives toluene on dry distillation, and benzoic acid on oxidation with potassium permanganate.

Cellulose Acetates.—Cellulose acetate was first prepared by heating cellulose with acetic anhydride at a high temperature.[2] Cross and Bevan[3] obtained the acetate by treating mercerized cellulose, or cellulose regenerated from its thiocarbonate, with acetyl chloride below 30° and a catalyzer such as zinc acetate or magnesium acetate. The cellulose acetate was soluble in chloroform and gave transparent elastic films. Their view[1] that the product was a tetracetate was based on a faulty method of analysis.[2] Unless there is hydrolysis of the cellulose, no derivative higher than the triacetate is obtainable.

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[1] A. Nastjukoff, *J. Russ. Phys.-Chem. Soc.*, **34** (1902), 231, 505; *Z. Farben-Ind.*, **6** (1907), 70.

[2] M. P. Schützenberger and L. Naudin, *Compt. rend.*, **68** (1869), 814.

[3] C. F. Cross and E. J. Bevan, G. P. 85329 (1894) and 86368 (1895).

Lederer[3] prepared cellulose acetate by acetylating Girard's hydrocellulose; also by first treating the cellulose with acetic acid and a little sulphuric acid at 60 to 70°, cooling, adding acetic anhydride, and allowing the reaction to proceed at room temperature.[4] Bayer and Company[5] employed a mixture of acetic acid, acetic anhydride, and sulphuric acid at a temperature below 50°. The acetates obtained by the two latter methods are identical and considered by Ost[6] as the triacetate of a hydrocellulose, $(C_6H_{10}O_5)_6.H_2O$ or $C_{36}H_{62}O_{31}$. The compound contained only 18 acetyl groups and not 19 or 20 as would be required if one molecule of water had combined through hydrolysis.

It is impossible to arrive at a definite decision regarding the presence of a molecule of water in a cellulose aggregate of the dimensions of C_{36} by ultimate analysis; nor is there a method for determining acetyl groups which is sufficiently reliable for this same purpose.

Formula	Acetic acid for		
	Diacetate, per cent	Triacetate, per cent	Tetracetate, per cent
$(C_6H_{10}O_5)_6$	48.76	62.47	72.70
$(C_6H_{10}O_5)_6 \cdot H_2O$	48.17	61.83	72.05

Schwalbe[7] came to the conclusion that the cellulose acetates of Bayer and Company and of Lederer were identical, and were derivatives of hydrocellulose, owing to their reducing properties.

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[1] C. F. Cross and E. J. Bevan, "Researches" (1895–1900), p. 80; *cf.* L. Vignon and F. Gerin, *Compt. rend.*, **131** (1900), 590.

[2] H. Ost, *Z. angew. Chem.*, **19** (1906), 998.

[3] P. Lederer, G. P. 118538 (1899) and 120173 (1900).

[4] P. Lederer, G. P. 163316 (1901).

[5] F. Bayer and Company, G. P. 159524 (1901).

[6] H. Ost, *l.c.*

[7] C. G. Schwalbe, *Z. angew. Chem.*, **23** (1910), 433–441; **24** (1911), 1256–1260.

The copper numbers of the cellulose acetates were 5.1 to 6.3 and 6.1 to 6.6 respectively. Acetylation by the Bayer method is preceded by the formation of hydrocellulose. If the acetylation is interrupted after 5 to 10 minutes, the acetylated portion has a reducing action on Fehling's solution. The later stages of acetylation are without increase in reducing power. The products first formed by the Lederer process do not reduce Fehling's solution but do so towards the end of the reaction. Acetylation of the hydrocellulose proceeds at a far more rapid rate than the formation of hydrocellulose.

Hydrocellulose was acetylated readily by heating with acetic anhydride and acetic acid, without the presence of sulphuric acid, while with sulphuric acid mercerized cotton was acetylated more slowly than normal cotton.[1] Hydrocellulose and an alkali-cellulose, prepared by heating cellulose 48 to 72 hours with 25 per cent sodium hydroxide solution at 110 to 120° and washing, were esterified far more rapidly than normal cellulose.[2] When 5 grams of material were acetylated by heating at 70° with 25 grams of glacial acetic acid, 25 grams of acetic anhydride, and 2.5 grams of anhydrous zinc chloride, hydrocellulose and the alkali cellulose required only 2 hours for complete acetylation while normal cellulose required 20 hours. When 0.5 gram of sulphuric acid was used as the catalyzer and the acetylation conducted at room temperature, the acetates from cellulose and hydrocellulose appeared to be identical after 24 hours. Increasing the sulphuric acid to 1 gram, gave acetylated products almost entirely soluble in alcohol, cellobiose octacetate predominating.

Cellulose acetates insoluble in acetone are readily converted into soluble modifications by heating at temperatures above 100°, in the absence of water, with ethylacetate, benzene, acetone, alcohol, acetylene tetrachloride, and similar solvents.[3] Neutral salts may be used as catalyzers. In the complete absence of water the conversion reaction is greatly prolonged. By the use of bisulphates in the presence of water, the acetyl value of the esters is not lowered, nor is the copper number higher than for the insoluble form. Solutions of acetone-soluble cellulose acetates, in the presence of small quantities of catalysts, such as sulphuric acid and sulphoacetic acid, gel on standing.[1] The cellulose acetate is then insoluble in acetone, acetylene tetrachloride, and lactic acid esters. The reversal of the solubility of cellulose acetates is accompanied by only minor changes in the copper number, indicating that hydrolysis does not take place to any appreciable extent.

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[1] H. Ost and F. Westhoff, *Chem. Ztg.*, **23** (1909), 198.

[2] H. Ost and T. Katayama, *Z. angew., Chem.*, **25** (1912), 1467–1470.

[3] E. Knoevenagel, *Z. angew. Chem.*, **27** (1914), 505–509.

Between the cellulose acetates soluble in chloroform and those soluble in acetone, which are presumably hydrocellulose acetates, there is a whole series of intermediates. A slight physical or chemical change in the cellulose acetate produces very marked differences in the solubility of the ester and in the viscosity of its solutions.

Cellulose triacetate, which is soluble in chloroform and tetrachlorethane, shows an optical rotation of $[\alpha]_D = ca. -20°$ in these solvents, and $[\alpha]_D = ca. -50°$ in pyridine. Cellulose acetate deposits from its solution in tetrachlorethane large crystalline needles containing some of the solvent with which it apparently enters into molecular union.[2]

Nascent sulphuryl chloride has been found to be a very active catalyst for the acetylation of cellulose and to produce a minimum of change in the cellulose acetate.[3] Immerse 5 grams of filter paper in 20 cubic centimeters of glacial acetic acid and 20 cubic centimeters of acetic anhydride containing 0.32 gram of chlorine; then add 2 cubic centimeters of acetic anhydride containing 0.26 gram of sulphur dioxide, and stir. The mixture gelatinizes rapidly and solution is complete in 5 minutes. After an additional 5 minutes' stirring, add 20 cubic centimeters of chloroform, pour into an excess of water, and heat to expel the chloroform. On breaking up the resulting globules by stirring, the cellulose triacetate deposits as a fine powder, which is easily washed free from acid. The ester contains 62.4 per cent of acetic acid.

Wood cellulose, obtained by extracting wood with 40 per cent hydrochloric acid in the cold for 42 hours and precipitating with water, gives a cellulose triacetate producing brittle films.[4] Zinc chloride and sodium ethylsulphate may be used as catalyzers, but sulphuric acid is unsatisfactory. Sulphite pulp under appropriate conditions gives an ester suitable for films. With sulphuric acid, there is a great tendency to form products with a high copper number and approaching a tetracetyl derivative. An acetate soluble in acetone but insoluble in chloroform is obtained as follows: Treat 5 grams of sulphite pulp with a solution of 20 grams of 100 per cent acetic acid, 0.5 gram of water, and 0.5 gram of sodium bisulphate. Heat for 17 hours at 50 to 70°, cool, and add with stirring 25 grams of acetic anhydride. The temperature must not exceed 60°. After warming the viscous solution at 70° for about half an hour, the reaction is ended. Cool the mixture somewhat, add 5 to 6 cubic centimeters of water, and let stand at 50° for 65 to 70 hours; then precipitate the acetate by pouring the solution into an excess of water.

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[1] E. Knoevenagel and K. König, *Cellulosechemie*, **3** (1922), 113–122.

[2] K. Hess, *Z. angew. Chem.*, **37** (1924), 997.

[3] W. L. Barnett, *J. Soc. Chem. Ind.*, **40** (1921), 8–10T.

[4] E. Hägglund *et al.*, *Cellulosechemie*, **3** (1922), 13–19.

Nauck[1] considers that for the preparation of useful acetates from wood pulp the physical properties of the pulp are more important than the chemical. The pulp should be in a finely divided condition. Acetylation proceeds the more uniformly the greater the specific surface. In this respect cotton behaves better than wood pulp, and dissolves more homogeneously during acetylation.

Cellulose Nitrates.—The alleged monoesters of cellulose are shown by X-ray examination to be mixtures of esters and unchanged cellulose, products having the compostion of a monoester being accidental.[2] Acetylation and benzoylation of cellulose are surface reactions proceeding from the exterior to the interior of the fiber as the esters formed are removed. The speed of esterification depends more on the previous chemical and physical treatments to which the fiber has been subjected than on the degree of symmetry in the arrangement of the crystallites. Nitration and denitration are topochemical reactions, that is, take place as if in a homogeneous sytem. The denitrated fiber gives the same point diagram as the original fiber, showing that there has been no change in the position of the crystallites.

Cellulose treated with a mixed acid consisting of 2 parts of concentrated sulphuric acid and 1 part of concentrated nitric acid is nitrated in 1 hour at a temperature of 15 to 20°. In mixed acid, the highest nitration is obtained when the system is represented by $HNO_3 + n(H_2SO_4.H_2O)$ and the lowest when nitric acid is present in the form of the hydrate, $HNO_3.H_2O$.[1] The sulphuric acid, accordingly, performs the function of freeing the nitric acid from its hydrate. It was thought by Cross and Bevan[2] that sulphuric acid esters of cellulose were formed, and that these were decomposed on washing with the formation of nitric esters. This view has been shown to be incorrect.[3] In mixed acid, the characteristic action of each acid is retarded. Cellulose dissolves rapidly in concentrated sulphuric acid, solution being followed by hydrolysis. Nitric acid (91 to 95 per cent) rapidly forms insoluble nitrates containing 9.6 to 13.5 per cent of nitrogen, hydrolysis and oxidation following on prolonged standing.

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[1] W. Nauck, *Cellulosechemie*, **2** (1921), 61–63.

[2] R. O. Herzog and G. Londberg, *Ber.*, **57** (1924), 329–332.

Vieille,[4] using nitric acid of sp. gr. 1.430 to 1.502, found that the more concentrated the acid, the greater was the esterification of the cellulose. It was, accordingly, assumed by Zachias[5] and Justin-Mueller[6] that cellulose nitrates were adsorption compounds. The nitric acid was dehydrated by the sulphuric acid to nitrogen pentoxide which was adsorbed by the cellulose. This is not true since the nitration of cellulose does not follow an adsorption curve.[7] With increasing concentration of nitric acid, the nitration advances step by step and not gradually. Furthermore, the reaction is not reversible, no nitric acid being removable from the nitrated cellulose with water.

Knecht[8] obtained a labile cellulose nitrate which was apparently an adsorption compound, by treating cellulose with nitric acid of sp. gr. 1.415. Water decomposed the dried product with the formation of nitric acid and gelatinized cellulose. A nitric acid of higher specific gravity than 1.415 gave true esters. An addition compound is first formed which in an excess of acid passes into the ester by the elimination of water.[1]

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[1] A. Saposchnikoff, *Z. Schiess-u. Sprengstoff.*, **1** (1906), 453–456; K. Kullgren, *Ibid.*, **3** (1908), 146–149.

[2] C. F. Cross and E. J. Bevan, *Ber.*, **34** (1901), 2496.

[3] C. N. Hake and M. Bell, *J. Soc. Chem. Ind.*, **28** (1909), 457–464.

[4] Vieille, *Compt. rend.*, **95** (1882), 132–135.

[5] P. D. Zachias, *Z. Farben-und Textilchem.*, **2** (1903), 233–239.

[6] E. Justin-Mueller, *Kolloid-Z.*, **2** (1907), 49–51.

[7] A. Müller, *Kolloid-Z.*, **2** (1907), 173–175.

[8] E. Knecht, *Ber.*, **37** (1904), 549–552.

In the case of cellulose nitrates, the introduction of a nitric acid group results in an increment of 26.8 cubic centimeters in the molecular solution volume, while with polyatomic alcohols, such as glycerine, there is a decrease in the volume for each nitric acid group from the first to the third. The difference is explained by assuming a cyclic structure for cellulose.[2]

The various possible nitrates of cellulose, using a $(C_6H_{10}O_5)_4$ molecule, are as follows:

Cellulose	Formula	N, per cent
Dodecanitrate	$C_{24}H_{28}O_{20}(NO_2)_{12}$	14.16
Endecanitrate	$C_{24}H_{29}O_{20}(NO_2)_{11}$	13.50
Decanitrate	$C_{24}H_{30}O_{20}(NO_2)_{10}$	12.78
Enneanitrate	$C_{24}H_{31}O_{20}(NO_2)_9$	11.98
Octonitrate	$C_{24}H_{32}O_{20}(NO_2)_8$	11.13
Heptanitrate	$C_{24}H_{33}O_{20}(NO_2)_7$	10.19
Hexanitrate	$C_{24}H_{34}O_{20}(NO_2)_6$	9.17
Pentanitrate	$C_{24}H_{35}O_{20}(NO_2)_5$	8.04
Tetranitrate	$C_{24}H_{36}O_{20}(NO_2)_4$	6.77

A cellulose trinitrate should theoretically contain 14.16 per cent of nitrogen. Hoitsema[3] obtained a nitrate with 13.9 per cent of nitrogen by the use of pure, crystallized, anhydrous nitric acid. Lunge[4] obtained a cellulose nitrate containing 13.92 per cent of nitrogen with a mixed acid of the composition: H_2SO_4, 63.35 per cent; HNO_3, 25.31 per cent; H_2O, 11.34 per cent. After a few months, the nitrogen content dropped to 13.50 per cent, where it remained constant. The influence of water on the degree of nitration will be seen in the following table:

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[1] C. Haeussermann, *Z. Schiess-u. Sprengstoff.*, **3** (1908), 121–122; E. Knecht and A. Lipschitz, *J. Soc. Chem. Ind.*, **33** (1914), 116–122.

[2] C. F. Cross and E. J. Bevan, *Ber.*, **42** (1909), 2198–2204.

[3] C. Hoitsema, *Z. angew. Chem.*, **11** (1898), 173–174.

[4] G. Lunge, *J. Am. Chem. Soc.*, **23** (1901), 527–579.

INFLUENCE OF WATER ON NITRATION

Number	N, per cent	Soluble in ether-alcohol, per cent	Yield on cotton, per cent	Acid mixture, per cent		
				H_2SO_4	HNO_3	H_2O
1	13.65	1.50	177.5	45.31	49.07	5.62
2	13.21	5.40	176.2	42.61	46.01	11.38
3	12.76	22.00	.....	41.03	44.45	14.52
4	12.58	60.00	167.0	40.66	43.85	15.49
5	12.31	99.14	159.0	40.14	43.25	16.61
6	12.05	99.84	153.0	39.45	42.73	17.82
7	11.59	100.00	156.5	38.95	42.15	18.90
8	10.93	99.82	144.2	38.43	41.31	20.26
9	9.76	74.22	146.0	37.20	40.30	22.50
10	9.31	1.15	138.9	36.72	39.78	23.50
11	8.40	0.61	131.2	35.87	38.83	25.30
12	6.50	1.73	.....	34.41	37.17	28.42

The solubility of cellulose nitrates shows considerable variation.

SOLUBILITY OF CELLULOSE NITRATES*

N, per cent	Solubility in		
	Acetone, ethylacetate, amylacetate, per cent	Ether-alcohol 2:1, per cent	Absolute alcohol, per cent
13.1–13.4	95–100	Insoluble	Insoluble
12.75–13.1	95–100	<30	Insoluble
12.5–12.75	95–100	50–100	<10
12.0–12.5	95–100	95–100	<50
11–12	95–100	90–100	50–100
10–11	95–100	80–100	<50
9–10	30–90	30–900	Insoluble
7–9	<30	<30	Insoluble
3–7	Insoluble	Insoluble	Insoluble

* ULLMANN, "Enzyk," **5** (1917), 96.

Nitrates prepared from cotton and viscose showed practically identical nitrogen contents and solubilities in ether-alcohol mixture.[1]

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[1] A. LUSK and C. F. CROSS, *J. Soc. Chem. Ind.*, **19** (1900), 642–644.

In the presence of strong nitric acid the nitrogen content of the cellulose increases to a maximum and then decreases. This denitrification results in the formation of oxycellulose.[1] Vignon[2] obtained identical cupric reducing values for oxycellulose nitrates and cellulose nitrates.

Strongly bleached cotton gave nitrates with 9.80 to 10.37 per cent of nitrogen in comparison with 11.8 to 11.92 per cent of nitrogen for cotton of high quality.[3] The oxycellulose esters obtained by nitrating strongly bleached cotton produce a decrease in viscosity of normal esters. The addition of definite amounts of such solutions of low viscosity to a cellulose nitrate solution of high viscosity caused a reduction in viscosity out of all proportion to the addition.[4]

Solutions of cellulose nitrates of low viscosity may be obtained by using mercerized cellulose, hydrocellulose, and cellulose that has been modified by heating.[5] Absorbent cotton was heated at 100° for 60 hours in atmospheres of oxygen, hydrogen, and carbon dioxide. The outflow times of acetone solutions of nitrates prepared from the celluloses so heated were 463, 1063, and 1110 seconds respectively, while a nitrate solution prepared from the unheated cotton gave a reading of 23330 seconds.

Cellulose treated with nitric acid of sp. gr. 1.473 to 1.50 passes into solution with the formation of xyloidins.[6] Preparation: Ten grams of cotton are saturated with water, pressed to a weight of 20 grams, and introduced with good cooling and stirring with a thermometer into 300 cubic centimeters of nitric acid of sp. gr. 1.50. The temperature rises to 25 to 30° but sinks rapidly with good cooling. The cellulose dissolves very rapidly and uniformly, but not completely. There is obtained about 315 cubic centimeters of a yellow, honey-like liquid. The initially high viscosity decreases rapidly. Water precipitates snow-white films containing 8.8 per cent of nitrogen.[7]

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[1] E. Knecht and A. Lipschitz, *J. Soc. Chem. Ind.*, **33** (1914), 117.

[2] L. Vignon, *Compt. rend.*, **131** (1900), 509–511.

[3] R. Namias, *Mon. sci.*, **8** (1918), 5–6; *cf.* C. Piest, *Z. angew. Chem.*, **21** (1908), 2497–2499.

[4] C. Piest, *Z. angew. Chem.*, **26** (1913), 24–30.

[5] E. Berl, *Z. Schiess-u. Sprengstoff.*, **4** (1909), 81–83.

[6] C. Hauessermann, *Z. Schiess-u. Sprengstoff.*, **1** (1906), 39; **3** (1908), 305.

[7] H. Jentgen, *Z. angew. Chem.*, **25** (1912), 945.

In nitric acid of sp. gr. 1.450 to 1.463, cotton fibers swell strongly, disintegrate, and pass into solution. Water produces almost complete precipitation, giving a product containing 6.5 to 8.0 per cent of nitrogen.[1] Acid of sp. gr. 1.469 to 1.476 gives a viscous fluid, xyloidin, containing 8 to 9 per cent of nitrogen, which is insoluble in acetone and ether-alcohol mixture. With acid of sp. gr. 1.48 to 1.50, cotton without noticeable structural change gives pyroxylin containing 9 to 12.5 per cent of nitrogen. Sulphite pulp behaves similarly, giving with acid of sp. gr. 1.495 a product with 11.1 per cent of nitrogen.[2] Acids of higher density have a strong parchmentizing action. Xyloidins, cellulose nitrates, and cellulose acetates, on standing in concentrated nitric acid for 3 to 4 months, are completely decomposed into water-soluble products.[3] Acetylcellulose on standing in fuming nitric acid for 14 days gave, presumably, a hydrocellulose nitrate containing 11.5 per cent of nitrogen.[4]

Cellulose nitrate dissolves rapidly on shaking with cuprammonium solution.[5]

Ammonium sulphide is one of the most efficient denitrating agents for cellulose nitrates.[6]

Collodion, treated with 10 per cent sodium hydroxide in the cold for 2 hours, is decomposed with the formation of oxypyruvic acid, $CH_2OH.CO.COOH$, which yields a yellow osazone.[7] Phenylhydrazine reacts with acetylcellulose nitrate to give the compound $C_{24}H_{28}O_7(NO_3)_4.(CH_3.COO)_8.HN_2.C_6H_5$.[8] Alcoholic sodium hydroxide acting on cellulose nitrate gave 7 to 8 per cent oxypyruvic acid, and cellulose tetranitrate, the latter reacting with phenylhydrazine to give $C_{24}H_{36}O_{15}.(NO_3)_4.NH_2.C_6H_5$. The osazone of oxypyruvic acid forms lustrous, blue-black needles from benzene; m.p. 215 to 216°.

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[1] C. Hauessermann, *Z. angew. Chem.*, **23** (1910), 1761–1763.

[2] C. Hauesserann, *Z. angew. Chem.*, **26** (1913), 456.

[3] C. Haeussermann, *Z. Schiess-u. Sprengstoff.*, **2** (1907), 426.

[4] C. Haeussermann, *Chem. Ztg.*, **29** (1905), 667.

[5] B. Rassow and W. von Bongé, *Z. angew. Chem.*, **21** (1908), 732.

[6] C. Piest, *Z. angew. Chem.*, **23** (1910), 1009; E. Knecht and A. Lipschitz, *J. Soc. Chem. Ind.*, **33** (1914), 122.

[7] W. Will, *Ber.*, **24** (1891), 400–407.

[8] E. Berl and W. Smith, *J. Soc. Chem. Ind.*, **27** (1908), 537.

Nitrates from Wood Pulp.—A nitrate of wood was prepared by Schultze[1] in 1865. Wood in the form of small, thin squares was boiled in soda solution, washed, steamed, treated with chlorine or bleaching powder, and nitrated with a mixture of 100 parts sulphuric acid and 40 parts nitric acid. This compound was long used as a sporting powder. Muschamp[2] cooked hardwoods with sodium hydroxide, obtaining what was virtually a lignin-free pulp, which was then nitrated.

Guttmann,[3] in 1894, stated that wood cellulose was not used for explosives, since it did not seem to give as tough a powder as guncotton. Years later Tedesco,[4] as a result of comparative tests on the stability of cotton and wood pulp which had been nitrated with mixed acid of varying composition, came to the conclusion that wood pulp was too unstable for explosives. The cotton nitrates ignited at 181 to 190° and the wood pulp nitrates at 138 to 153°. On the other hand, Nitznadel[5] concluded that the nitrates from sulphite pulp were well suited for explosives, the stability tests running above the minimum limit of 180°. The chief disadvantages of wood-pulp nitrates in comparison with cotton nitrates were the higher solubility in ether-alcohol, lower yields, and somewhat lower ignition temperature.

De Mosenthal[6] found the following properties for nitrated wood cellulose:

WOOD CELLULOSE NITRATES

Number	N, per cent	Solubility alcohol-ether * per cent	Density
15	13.30	10	1.715
16	12.80	98	1.659
17	12.50	95	1.673

* Two volumes ether (sp. gr. 0.72) and one volume alcohol (sp. gr. 0.76).

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[1] E. SCHULTZE: cited by R. ESCALES, "Die Schiessbaumwolle," Leipzig (1905), p. 264.

[2] J. B. MUSCHAMP, *Ber.*, **5** (1872), 122.

[3] O. GUTTMANN, *J. Soc. Chem. Ind.*, **13** (1894), 576.

[4] H. TEDESCO, *Z. Schiess-u. Sprengstoff.*, **7** (1912), 474–477.

[5] K. A. NITZNADEL, *Z. Schiess-u. Sprengstoff.*, **7** (1912), 257–260, 301–305 339–343, 384–387; *Wochbl. Papierfabr.*, **43** (1912), 3488–3489.

[6] H. DE MOSENTHAL, *J. Soc. Chem. Ind.*, **26** (1907), 443–450.

Wood-pulp Nitrates[1]

Pulp	Analysis of wood pulp							Analysis of wood-pulp nitrate				
	Moisture, per cent	Ash, per cent	Copper number corrected	Hydrolysis number	Residue from Na_2S, per cent	Pentosan, per cent	Methoxyl, per cent	Nitrogen, per cent	Soluble ether-alcohol, per cent	Free cellulose, per cent	Ignition temperature, degrees Centigrade	Yield from 100 grams pulp, grams
Sulphite pulp:												
1. Nitrating paper	5.87	0.65	0.55	9.94	95.4	1.60	0.65	12.93	7.76	0.71	185	150
2. Aspen	7.11	0.45	3.17	14.32	79.9	6.43	0.84	13.08	11.58	0.03	185	118.3
3. Mitscherlich, hard	8.96	0.38	1.95	12.52	83.5	4.36	0.90	11.88	31.36	1.25	184	118.3
4. Ritter-Kellner, bleached	7.68	0.35	2.68	11.01	78.5	3.32	0.76	13.15	12.69	0.04	183	130
Soda pulp:												
5. Pine	10.97	1.25	....	10.62	97.3	5.94	0.92	12.81	23.00	1.78	183	143.5
6. Cotton, purified	7.21	0.11	0.29	7.35	99.5	6.94	0.44	13.21	5.71	0.46	183	158.3

[1] A. Schrimpff, "Nitrocellulose aus Baumwolle und Holzzellstoffen," München (1919), 158 pp.

The optical rotations of the nitrates in ethylacetate and acetone were $[\alpha]_D = +23.3$ to $+23.6°$. Number 16 was without action on polarized light.

Comparative nitrations of cotton and various wood pulps were carried out by Schwalbe and Schrimpff.[1] The highest nitrate obtained from wood pulp contained 13.34 per cent of nitrogen, and that from cotton, 13.46 per cent of nitrogen. A nitrated wood pulp could be prepared having a solubility of 5 to 6 per cent in alcohol-ether. No difficulty was met with in removing the unstable impurities, so that the wood pulp nitrates would correspond in stability to cotton nitrates. Sulphuric esters were best eliminated from the nitrated product by boiling with 1 per cent hydrochloric acid.

Coniferous pulps are superior to hardwood pulps owing to their longer fibers and lower percentage of hemicelluloses.[2] Soda pulps both from hardwoods and softwoods should be used in the unbleached condition, since bleaching does not permit them to fall within the government specification, that the solubility in boiling 10 per cent potassium hydroxide shall not exceed 10 per cent. The presence of dark-colored products, which are not removable from the soda pulp by digestion with sodium hydroxide, results in a dark cellulose nitrate, but this feature is not considered objectionable. The solubility of sulphite pulp in potassium hydroxide, while high originally, is not increased by bleaching. Previous to nitration, the sulphite pulp is purified by heating with a 2 per cent solution of sodium hydroxide at 115° until the alkalinity disappears.[3] The loss in weight, which is about 25 per cent, is due to the removal of hemicelluloses, modified celluloses, lignin residues, and resin. It is then treated with about 4 per cent of bleach. In the form of crêpe sheets both soda and sulphite pulps nitrated evenly, giving products with a high nitrogen content. The yield was 150 per cent, compared with 160 to 165 per cent with cotton. The wood-pulp nitrates were more difficult to dehydrate than the cotton nitrates.

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[1] C. G. Schwalbe and A. Schrimpff, *Z. angew. Chem.*, **27** (1914), 662–664.

[2] S. D. Wells and V. P. Edwards, *Paper* **25,** 23 (1919), 180–185.

[3] V. P. Edwards, U. S. P. 1310694 (1919).

According to Schwarz,[1] the most suitable wood pulp for nitration is made by the Ritter-Kellner process. Wood cellulose is more voluminous than cotton cellulose, so that the nitrating charge is reduced 10 per cent. It is less adsorbent to acid, and the acid is not washed out as readily as from cotton. In all other respects, however, wood pulp is superior to cotton.

Purification of Wood Pulps.—Sulphite pulp can be rendered inactive towards Fehling's solution by boiling with milk of lime.[2] During the treatment, half of the pentosans are destroyed. Lime has little action on soda pulp. This would be expected from the drastic alkaline treatment by which it is produced. Ten grams of unbleached sulphite pulp boiled with 3 grams of barium oxide for 3 hours showed a utilization of 13.7 per cent of barium oxide; and after 8 hours' boiling, a utilization of 13.4 per cent of barium oxide based on the pulp. The loss in weight of the pulp was 16.2 and 17.0 per cent. Pure cotton showed no loss on boiling with lime water.[3]

Harding[4] heated wrapping paper—probably kraft pulp—with a 1 per cent solution of sodium hydroxide at 102° for 30 hours, whereby the pulp lost 40 per cent in weight, but still contained lignin. As would be expected, sodium sulphide (50 grams in 200 cubic centimeters of water) attacks sulphite pulps more strongly than soda pulps. Aspen, though cooked by the soda process, is an exception, being strongly attacked by this reagent.[5]

Opfermann[6] purifies wood pulp by boiling it for 3 to 6 hours at 2 to 3 atmospheres' pressure with a 0.5 to 2.0 per cent solution of sodium carbonate. The addition of a small amount of alkali hydroxide or sulphide increases the softness and absorbency. The pulp may also be purified with a solution containing 10 grams of lime per liter. The efficiency of alkaline earth oxides is increased in the presence of salts of oxyacids, in which, these oxides are more soluble than in water.[1]

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[1] R. Schwartz, *Oesterr. Chem. Ztg.*, **22** (1919), 50–52, 57–60.

[2] C. G. Schwalbe and E. Becker, *J. prakt. Chem.*, **100** (1919), 19–47.

[3] M. Robinoff, Diss. Darmstadt (1912).

[4] W. G. Harding, *J. Phys. chem.*, **25** (1921), 201–203.

[5] C. G. Schwalbe, *Z. angew. Chem.*, **31** (1918), 53.

[6] E. Opfermann, G. P. 219085 (1909); F. P. 402462 (1909); *cf.* C. Piest, *Papier-Fabr.*, **12** (1914), 860–865.

Pulps produced by alkaline processes are purified by boiling with a sulphite solution.[2] Pentosans and lignin can be almost completely removed by boiling the bleached pulp with a sulphite solution and again bleaching.[3]

Another method for rendering wood pulp similar to cotton, and suitable for cellulose nitrate and artificial silk, consists in treating it with oxidizing agents, such as gaseous oxides of nitrogen, nitrous acid, nitric acid, perchloric acid, etc., followed by boiling with an alkaline solution.[4]

Drewsen[5] purifies wood pulp for nitration purposes by bleaching with 2 to 8 per cent of chlorine, then boiling with dilute sodium carbonate or sodium hydroxide until the pulp shows a solubility in potassium hydroxide of less than 7 per cent. To remove resins and incrusting substances, Schonlau[6] treats bleached wood pulp in a beating engine with a hot emulsion of water and turpentine. Resinous impurities on nitration, form yellow compounds which reduce the stability of the cellulose nitrate.[7] They also prevent uniform penetration of the nitrating mixture. The ether-alcohol extract should not exceed 0.4 per cent. Sulphite pulp, freed from resinous impurities, oxycellulose, and hydrocellulose, by boiling with dilute alkali, gives a nitrate very similar to cotton nitrate.

Straw and wood pulps high in pentosans contain, after nitration, correspondingly high amounts of unnitrated material.[8] The pentosans appear to form a coating which resists penetrance by the mixed acid.

It is important that the wood pulp contain a high percentage of α-cellulose. That this result is attained by suitable purification, is shown by the following:[9]

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[1] C. G. Schwalbe and E. Becker, G. P. 36906 and 371507 (1919); E. L. Rinman, G. P. 301587 (1917).

[2] W. Schacht, G. P. 306366 (1918).

[3] C. G. Schwalbe, G. P. 378260 (1921).

[4] C. G. Schwalbe, F. P. 410460 (1909).

[5] V. Drewsen, U. S. P. 1283113 and 1283114 (1918).

[6] K. Schonlau, F. P. 469484 (1914).

[7] W. E. B. Baker, Tech. Assoc. Pulp and Paper Ind., N. Y., Feb. 6–7 (1918), 45–47.

[8] B. Rassow and E. Dörr, *J. prakt. Chem.*, **108** (1924), 113–186.

[9] R. G. Woodbridge, *J. Ind. Eng. Chem.*, **12** (1920), 380–384.

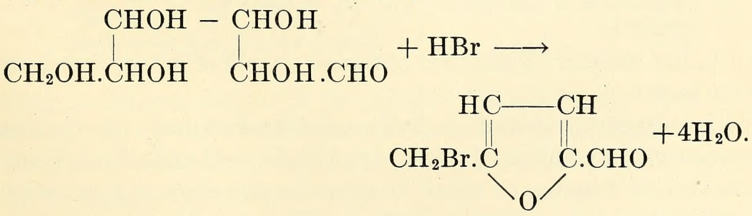
Fiber	α-Cellulose, per cent	β-Cellulose, per cent	γ-Cellulose, per cent
Purified cotton....................	94.5	3.0	2.5
Mildly bleached spruce sulphite digested 5 hours at 80 pounds pressure with 2 per cent NaOH solution.....................	95.0	2.0	3.0
Unbleached spruce sulphite purified as above........................	94.5	2.0	3.5

Mechanical difficulties in preparing the cellulose nitrate are overcome by mixing the purified pulp with 50 per cent of cotton. This procedure has been protected by Claessen.[1]

Hydroxymethylfurfural.—When hexose carbohydrates are treated with the hydrogen halides in an indifferent solvent such as ether or chloroform, ω-brommethylfurfural is obtained; it crystallizes in orange-yellow prisms of m.p. 59.5 to 60.5°. The reaction is preferably carried out by adding to the carbohydrate, chloroform saturated with hydrogen bromide and heating in a water bath for 2 hours. The corresponding chlorine derivative is obtained with hydrogen chloride.[2]

In the formation of the aldehyde from cellulose, the latter is first hydrolyzed to glucose. Hess[3] assumes that the hydrogen bromide combines first with the glucose. This compound then decomposes with the elimination of three molecules of water to give hydroxymethylfurfural, with which the hydrogen bromide reacts to give ω-brommethylfurfural, as shown above.

$$(C_6H_{10}O_5)_n + nH_2O = nC_6H_{12}O_6$$



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[1] C. Claessen, G. P. 300844 (1915).

[2] H. J. Fenton and M. Gostling, *J. Chem. Soc.*, **73** (1898), 554; **75** (1899), 423; **79** (1901), 361; **95** (1909), 1334.

[3] K. Hess, *Z. Elektrochem.*, **26** (1920), 234.

Since fructose gave high yields of Br-methylfurfural in comparison with glucose, it was assumed that the reaction was a criterion for carbohydrates with a ketonic structure.[1] Hibbert[2] has recently shown that the reaction is of no value for this purpose, the high yields from cellulose (56 per cent) in comparison with glucose (12 per cent) being due largely to the absence of free aldehyde groups that may interfere with the reaction. The yields of Br-methylfurfural from 10-gram samples of various carbohydrates are given below:

Material	Yield of ω-brom-methylfurfural	
	Grams[1]	Grams[2]
Swedish filter paper	3.0	
Ordinary cotton	3.3	5.6
Mercerized cotton	2.1	
Viscose	...	5.5
Straw cellulose	2.3	
Lævulose	2.2	1.2
Dextrose	0.33	1.2
Galactose	0.34	0.3
Cane sugar	0.85	3.5
α-Methylglucoside	....	1.5
Cellobiose	....	2.7

[1] H. J. Fenton and M. Gostling, *J. Chem. Soc.*, **79** (1901), 361.
[2] H. Hibbert, *l.c.*

In similar manner, Erdmann[3] obtained a yield of 3.7 per cent from filter paper.

Kiermayer[4] prepared a hydroxymethylfurfural, by heating sucrose with a solution of 0.3 per cent oxalic acid at 3 atmospheres' pressure for 3 hours, to which he gave the structure of β-hydroxy-δ-methylfurfural; oxime, m.p. 77 to 78°; phenylhydrazone, m.p. 138°. Van Ekenstein[5] accepted this constitution, but later[6] stated that the aldehyde prepared by Kiermayer's method was ω-hydroxymethylfurfural. Fenton had previously shown that his bromine compound was ω-brommethylfurfural.

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[1] H. J. Fenton and M. Gostling, *l.c.*

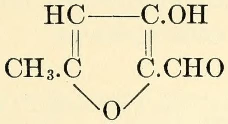
[2] H. Hibbert and H. S. Hill, *J. Am. Chem. Soc.*, **45** (1923), 176–182.

[3] E. Erdmann, *Ber.*, **43** (1910), 2391–2398.

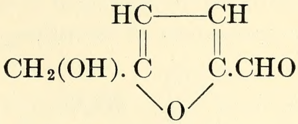
[4] J. Kiermayer, *Chem. Ztg.*, **19** (1895), 1003; *cf.* G. Dull, *Ibid.*, 166, 216.

[5] W. A. van Ekenstein and J. J. Blanksma, *Chem. Weekblad*, **6** (1909), 217.

[6] *Chem. Weekblad*, **6** (1909), 1047; *Ber.*, **43** (1910), 2355.



β-Hydroxy-δ-methylfurfural



ω-Hydroxymethylfurfural

Erdmann[1] then prepared ω-hydroxymethylfurfural by treating ω-brommethylfurfural with silver acetate. The aldehyde gave a semioxamazone, $C_6H_6O_2.N.NH.CO.CO.NH_2$, m.p. 216°, while Kiermayer's aldehyde gave a semioxamazone having no definite melting point, but decomposing at about 260°. It was found that ω-hydroxymethylfurfural, owing to the labile hydroxyl group, could be transformed into the Kiermayer isomer by heating with aqueous oxalic acid under pressure, or by overheating during its preparation. The Kiermayer aldehyde is also obtained in the dry distillation of cellulose.[2]

Heuser[3] obtained the following yields of hydroxymethylfurfural, using a 5 per cent solution of oxalic acid at 180° for half an hour. In this incident, the presence of free carbonyl groups (hydrocellulose) improved the yield of the aldehyde. According to Heuser, the semioxamazone of Kiermayer's aldehyde melts at 235 to 236°, and the phenylhydrazone at 140°, not 137° as given[4] by Kiermayer and Erdmann.

	Hydroxymethylfurfural Per Cent
Cotton	0.82
Viscose	5.16
Hydrocellulose (Knoevenagel)	10.84

Aldohexoses, heated with aqueous oxalic acid, gave a yield of only 1.0 per cent of hydroxymethylfurfural in comparison with 20 to 25 per cent from the ketohexoses.[5] As little as 0.001

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[1] E. Erdmann, *l.c.*

[2] E. Erdmann and C. Schaefer, *Ber.*, **43** (1900), 2404.

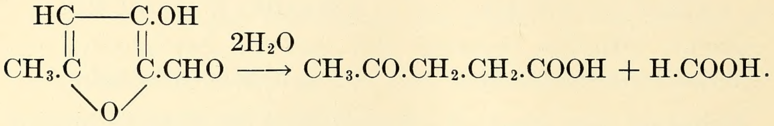
[3] E. Heuser and W. Schott, *Cellulosechemie*, **4** (1923), 85; *cf. Ibid.*, 25.

[4] According to B. Tollens (*Ber.*, **37** (1904), 303), the m.p. is 140 to 141°.

[5] W. A. van Ekenstein and J. J. Blanksma, *Ber.*, **43** (1910), 2355.

milligram of the aldehyde can be detected by means of the red precipitate formed with resorcinol and concentrated hydrochloric acid.

Hydroxymethylfurfural is apparently an intermediate product in the formation of lævulinic acid from carbohydrates.



It reduces Fehling's solution readily, and to twice the extent of glucose.

CHAPTER X

SACCHARIFICATION OF CELLULOSE AND WOOD

Saccharification is of more narrow scope than hydrolysis and refers to the conversion of cellulose to the simple sugars. In the case of "sulpholysis", hydrolysis and formation of dextrin esters of sulphuric acid take place simultaneously. Saccharification always appears to take place through the intermediate formation of dextrins.

Saccharification of Cellulose with Concentrated Acids.—In 1819, Braconnot[1] dissolved linen in sulphuric acid of sp. gr. 1.827. After standing some time, the solution was diluted, boiled, the acid removed with lime, and the sugar solution carried to dryness. In this way 23.3 grams of sugar were obtained from 20.4 grams of linen, so that the yield presumably was quantitative. A crystalline, fermentable sugar identical with glucose was isolated.

Numerous subsequent attempts have been made to obtain a quantitative conversion of cellulose to glucose. Flechsig[2] dissolved cotton in 69 per cent sulphuric acid, let the solution stand 45 minutes, diluted to an acid concentration of 2.5 per cent, and boiled for 5 to 6 hours. Reduction with Fehling's solution showed 96.9 per cent of glucose, based on the cellulose. Crystalline glucose was obtained, though the yield was not quantitatively determined. Ost and Wilkening[3] confirmed Flechsig's results. They obtained from 90 to 95 per cent of the theoretical yield of sugar as determined by the cupric reducing value. Fermentation showed 80 to 83 per cent of the apparent dextrose values.

In repeating Flechsig's work, Schwalbe and Schulz[4] threw doubt on the high yields of sugar reported, it having been found that the reducing value was not a reliable indication of the amount of glucose present. An appreciably higher reduction was obtained when the acid was neutralized with barium carbonate than with sodium hydroxide. In some cases a high reducing value was apparently due in considerable part to dextrins; in others, a high yield of sugar could be obtained, though the reducing value was low. Artificial mixtures of Guignet's soluble cellulose and glucose showed abnormally low reducing values. Storer[1] had 10 years previously called attention to the error involved in assuming that in hydrolyzing cellulose the reducing value could be quantitatively referred to glucose.

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[1] H. Braconnot, *Ann. chim. phys.*, [2] **12** (1819), 172; **25** (1827), 81.

[2] E. Flechsig, *Z. physiol. Chem.*, **7** (1883), 528.

[3] H. Ost and L. Wilkening, *Chem. Ztg.*, **34** (1910), 461.

[4] C. G. Schwalbe and W. Schulz, *Ber.*, **43** (1910), 916.

Mühlmeister[2] used Flechsig's method on various celluloses. Using 70 per cent sulphuric acid, cotton gave 104.8 per cent of glucose by reduction, and 79 per cent of the theoretical yield of alcohol; Ritter-Kellner sulphite pulp gave 90.6 per cent of glucose by reduction, and 83.1 per cent of the theoretical yield of alcohol. By a similar procedure, Neuman[3] obtained 87 to 91 per cent of glucose as determined by fermentation and the polariscope.

The results of Monier-Williams[4] leave no doubt of a possible quantitative saccharification of cellulose, since he obtained 90.67 per cent of the theoretical amount of crystalline glucose. Ten grams of cotton, having 6.93 per cent moisture and 0.13 per cent ash, were dissolved in 50 cubic centimeters of 72 per cent sulphuric acid and allowed to remain at room temperature for 1 week. The acid was diluted to 5 liters and boiled under a reflux condenser for 15 hours. The liquid was filtered, neutralized with barium carbonate, filtered, and the filtrate evaporated to dryness at reduced pressure (40 millimeters). To take care of the alkalinity that developed during evaporation, a few drops of methyl red were added and the solution kept neutral by the repeated addition of $0.1N$ sulphuric acid. The residue was extracted with methyl alcohol free from acetone. After filtration and decolorization with a little animal charcoal, the solvent was evaporated in a current of dry air at a low temperature. There were obtained 9.718 grams of nearly white crystals.

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[1] F. H. Storer, *Bull. Bussey Inst.*, **2** (1900), 463.

[2] H. Mühlmeister, "Beiträge zur Hydrolyse und Sulfolyse der Zellulose," Diss. Hannover (1913), p. 11.

[3] J. Neuman, "Kritische Studien über Hydrolyse der Cellulose und des Holzes," Dresden (1910), p. 34.

[4] G. W. Monier-Williams, *J. Chem. Soc.*, **119** (1921), 803–805.

Sulphuric acid of 70 per cent concentration is, according to Ost,[1] more suitable for the sulpholysis of cellulose than a stronger acid. It forms dextrin esters of sulphuric acid which on dilution and subsequent heating at 120° may be almost quantitatively hydrolyzed to glucose. Any "amyloid" formed on dilution must be redissolved in strong acid before it can be hydrolyzed.

Strong sulphuric acid in time causes blackening of the carbohydrates due to dehydration. Tschumanow[2] in this way prepared colloidal "carbon." Strips of filter paper were left in contact with concentrated sulphuric acid for 3 days and the dark-colored liquid obtained was diluted with a large volume of water. The precipitate, dried at 100 to 112°, contained 62.1 per cent C, 5.0 per cent H, and 32.9 per cent O. This corresponds with the formula $(C_2H_2O)_n$ and approaches ulmic acid in composition. When 2.59 grams of cellulose were dissolved in 100 cubic centimeters of concentrated acid and let stand 2½ years, a black, quivering, gelatinous mass was obtained. In a similar manner, gelatinous carbon and a stable colloidal carbon have been prepared from sugar.[3]

In 1880, Dauzivillé[4] described a method of hydrolysis in which moist cellulose was treated with hydrogen chloride gas until swelling and solution took place. After standing to further the hydrolysis, the hydrochloric acid was removed for the most part by suction, the residue strongly diluted, and boiled to produce sugar.

It was observed by Willstätter and Zechmeister[5] that hydrochloric acid of a specific gravity greater than 1.20 and containing 40 to 42 per cent of hydrogen chloride rapidly dissolved cellulose. When 1 gram of cotton was dissolved in 100 cubic centimeters of acid of sp. gr. 1.204 and let stand at 15 to 16° for 22 hours, the reducing value indicated 95.4 per cent, and the optical rotation 96.3 per cent, of the theoretical yield of glucose.

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[1] H. Ost, *Ann.*, **398** (1913), 320.

[2] S. Tschumanow, *Kolloid-Z.*, **14** (1914), 321–322.

[3] L. Sabbatini, *Kolloid-Z.*, **14** (1914), 29–31.

[4] E. S. Dauzivillé, G. P. 11836 (1880).

[5] R. Willstätter and L. Zechmeister, *Ber* **46** (1913), 2995–2998; L. Zechmeister, Diss. Zürich (1913), p. 37.

The rotatory power of glucose increases greatly with the strength of the acid. The following values were observed for 1 gram of glucose in 100 cubic centimeters of acid at 16 to 17°:

d 15°/4°	Per Cent HCl	$[\alpha]_D$
1.018	3.68	+54.5°
1.154	30.4	61.0
1.204	39.9	97.5
.....	44.5	164.6

The increased rotation was attributed to the formation of isomaltose. According to Daish,[1] the high rotation of dextrose in fuming hydrochloric acid is due to almost complete transformation of the sugar into the α-form, whose rotation is of the order $[\alpha]_D = +106°$. The course of the hydrolysis of cotton cellulose was followed by observing the rotation at intervals.[2] After 40 minutes, $[\alpha]_D$ was +1.0°, this value increasing to and becoming constant at 98.5° after 3100 minutes. When the rotation was plotted against time, a sharp break in the curve was noted between the second and the third hour.

The work of Willstätter and Zechmeister has been criticized by various investigators. Ost[3] objected to the claim of novelty in the use of hydrochloric acid and asserted that satisfactory evidence for quantitative saccharification cannot be obtained by the use of either Fehling's solution or the polariscope. Cunningham[4] showed that, contrary to previous opinion, hydrochloric acid forms esters with the degradation products of cellulose. It was also observed that celluloses varying so widely in composition as cotton and esparto gave identical rotations. In 40 per cent hydrochloric acid, cotton showed $[\alpha]_D = +56.8°$ after 2250 minutes; esparto cellulose, $[\alpha]_D = +46.3°$ after 2250 minutes, increasing to +54.4° after 3000 minutes. Slight variations in the concentration of the hydrochloric acid cause marked constitutional changes in the simple hexoses, as shown by the marked fluctuations in optical activity.

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[1] A. J. Daish, *J. Chem. Soc.*, **105** (1914), 2053.

[2] L. Zechmeister, *l.c.*

[3] H. Ost, *Ber.*, **46** (1913), 2995.

[4] M. Cunningham, *J. Chem. Soc.*, **113** (1918), 173–181.

It is not apparent how celluloses containing pentosans can give the same rotation as cotton. The xylan in esparto cellulose is changed to furfural in hydrochloric acid of high concentration.[1]

Cotton cellulose, and the celluloses of yellow birch, white spruce, and Douglas fir, isolated by chlorination, when dissolved in 41 per cent hydrochloric acid, were found by Sherrard and Froehlke[2] to give similar but not identical optical rotation curves (Fig. 7). In addition to the break in the curves between the second and third hours, another break occurred at about the seventh hour. Assuming that glucose is the only sugar formed during the hydrolysis, the amounts of sugar formed are practi-

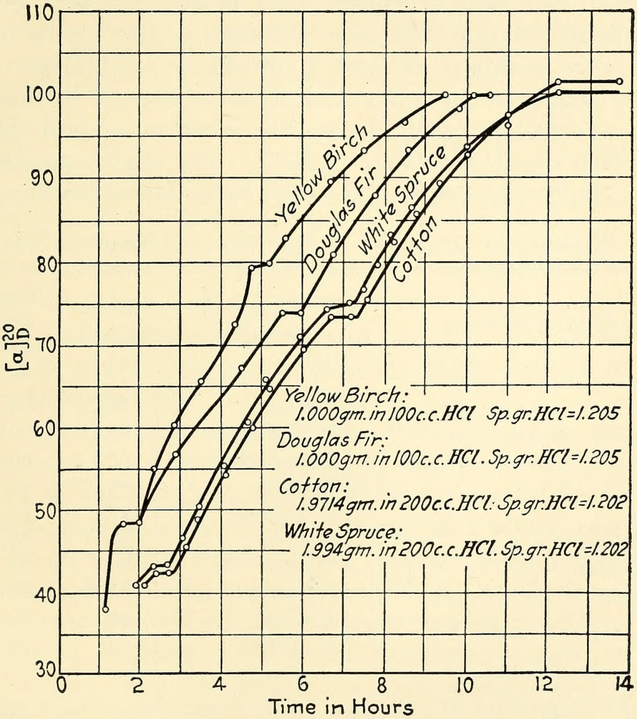

FIG. 7.—Change in specific rotation with time of hydrochloric acid solutions of various celluloses. (*After Sherrard and Froehlke.*)

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[1] E. L. HIRST and D. R. MORRISON, *J. Chem. Soc.*, **123** (1923), 3226.

[2] E. C. SHERRARD and A. W. FROEHLKE, *J. Am. Chem. Soc.*, **45** (1923), 1729–1734.

cally identical for the four celluloses, namely, 91.40 per cent for cotton to 90.10 per cent for birch cellulose. This is remarkable in view of the presence of mannan in spruce cellulose and of about 28 per cent of pentosan in birch cellulose.

Cellulose, when dissolved in a solution of one part of zinc chloride in two parts of concentrated hydrochloric acid, reaches a maximum rotation and then decreases.[1] No breaks in the curves were obtained as with hydrochloric acid alone. The different celluloses showed a considerable variation in rotation. In the solvent employed, the specific rotation for pure glucose was +60.0°, and for xylose +32.0°. The higher rotation of cotton cellulose was attributed to the formation of dextrins.

Optical Rotation of Cellulose in Zinc Chloride-Hydrochloric Acid

Kind of cellulose	Method of isolation	Time, hours	Maximum specific rotation
Cotton	J. König	72.5	+82.55°
Cotton	B. Tollens	78	72.02
Cotton	Cross and Bevan	55	56.72
Jute	J. König	56.5	71.50
Jute	B. Tollens	49	71.57
Hydrocellulose	Girard	24	45.02 (?)
Oxycellulose	Vignon	30	52.29
Fir	J. König	71.5	60.51
Beech	J. König	38	62.00
Beech	H. Müller	24	48.84

Krull[2] found that 97 per cent of the theoretical yield of glucose could be obtained from cotton by hydrolysis with strong hydrochloric acid. The glucose present was determined with Fehling's solution. The cellulose, containing three parts of water, was treated with hydrogen chloride gas until saturated. Hydrolysis was allowed to proceed for 5 to 18 hours at 20°. By means of a vacuum, the hydrochloric acid content was then reduced to 2 per cent. The solution, reduced to a cellulose content of 1 to 10 per cent by dilution with water, was boiled for 8 to 10 hours to complete the hydrolysis. (Krull states that the data given in the table below were obtained by means of a primary hydrolysis lasting 20 hours, followed by diluting and boiling for 8 hours; in another paper[1] where the same data are given, it is stated that the primary hydrolysis lasted 5 hours.) On extending the period of primary hydrolysis to 24 hours or beyond, "reversion" took place with the formation of relatively large amounts of non-fermentable products.

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[1] J. König and F. Hühn, "Bestimmung der Zellulose in Holzarten" (1912), 55.

[2] H. Krull, "Versuche über Verzuckerung von Zellulose," Diss. Danzig (1916), 62 pp.

Material	Sugar, per cent	Alcohol, per cent	Residue, per cent
Cotton	94.39	46.60	
Cotton	97.86	44.28	
Hydrocellulose (Girard)	13.2	Qual.	77.28
Sulphite pulp, unbleached	84.9	29.98	
Sulphite pulp, strongly bleached	70.43	14.0	
Soda pulp, unbleached	88.65	25.34	12.84

The cellulose, according to Kauko,[2] should contain two parts of water previous to saturation with hydrogen chloride. A larger amount of water reduces the yield of dextrose. At 13°, an 80 per cent yield of sugar can be obtained in 4 hours, and 90 per cent, in 40 hours. Vapor-tension measurements indicate that cellulose forms an addition product with hydrochloric acid, two mols of hydrogen chloride combining with each C_6 group.

Cotton in ordinary concentrated hydrochloric acid, after 40 hours' action, does not reduce Fehling's solution but does so after 87 hours.[3]

Boiling solutions of hydrofluoric acid, of concentrations of 0.5 to 30.0 per cent, act very slightly on cellulose. At the temperature of boiling water, acid of 40 to 50 per cent concentration gave in 6 hours, 41 per cent of glucose based on the weight of the cellulose. Further heating caused decomposition of the sugar.[4]

Saccharification of Cellulose with Dilute Acids.—The yield of dextrose by the hydrolysis of cellulose with dilute acids under pressure, is much lower than that obtained by the use of strong acids in the cold. A subsequent hydrolysis of the residue yields more sugar, but the yield is much reduced over the first. The low yield of sugar is due in part to the destruction of some of the sugar formed.

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[1] A. Wohl and H. Krull, *Cellulosechemie*, **2** (1921), 7.

[2] Y. Kauko, *Naturwissenschaften*, **9** (1921), 237–238.

[3] W. O. de Coninck, C. A., **5** (1911), 1585.

[4] J. Ville and W. Mestrezat, *Compt. rend.*, **150** (1910), 783–784.

Decomposition of sugar by acids produces for the most part formic and lævulinic acids, and humus substances. The destructive action of dilute sulphuric acid, under pressure, on glucose, is shown in the following table.[1]

Dextrose used (in 5 per cent solution), grams	Heated with 2.5 per cent H_2SO_4		Dextrose decomposed, grams	Found, referred to 100 grams of decomposed glucose		
	Temperature	Time, hours		Formic acid, grams	Lævulinic acid, grams	Humus, grams
20	145	7	15	16.2	32.4	13.3
40	145	5	26	17.4	40.2	12.3
20	145	3	7.5	13.4	30.3	8.0
40	145	1.5	13	17.8	32.2	8.5
40	120	8	11	16.9	44.0	8.2
40	120	3	4	8.6	8.1	0

The following results were obtained by Neuman:[2]

DECOMPOSITION OF 1 GRAM OF GLUCOSE IN 25 CUBIC CENTIMETERS OF SULPHURIC ACID OF VARIOUS CONCENTRATIONS HEATED FOR HALF AN HOUR AT THE CORRESPONDING TEMPERATURE

H_2SO_4, per cent	Per cent undecomposed glucose at T =			
	150°	160°	175°	185°
0.1	100	94.4	94.2	88.8
0.5	96.1	92.7	91.6	50.0
1.0	94.4	83.3	86.6	33.3
1.5	88.8	80.5	55.5	31.1
2.0	87.7	75.0	37.2	5.5
2.5	86.6	72.2	33.3	5.0
3.0	83.3	71.0	25.0	2.7
5.0	80.5	38.8	5.5	0.0

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[1] H. Ost and T. Brodtkorb, *Chem. Ztg.*, **35** (1911), 1126; *cf.* H. Ost and L. Wilkening, *Ibid.*, **34** (1910), 461.

[2] J. Neuman, *l.c.*, 31.

In the hydrolysis of cellulose a temperature of 175° should not be exceeded, since this is near the "critical point" for the decomposition of glucose. The decomposition of mannose is similar to that of glucose.[1]

Cotton, hydrolyzed six times in succession with 1 per cent sulphuric acid at 150° for 2 hours, gave a total reducing value equivalent to only 44.3 per cent of glucose.[2] Mühlmeister,[3] under the same conditions, obtained 12.3 and 8.7 per cent of glucose by two hydrolyses, making a total of 21.0 per cent. Two cooks with 2 per cent acid gave a total of 33.6 per cent of glucose. Neuman[4] treated cotton with 0.5 per cent sulphuric acid at 175° for 30 minutes, and repeated the hydrolysis on the undissolved portion:

1. Cotton	26.6 per cent glucose (on original)
2. Residue from (1)	15.0 per cent glucose (on residue)
3. Residue from (2)	12.0 per cent glucose (on residue)
4. Residue from (3)	13.3 per cent glucose (on residue)

The total yield of glucose by the four hydrolyses was 46.9 per cent based on the original cellulose.

The influence of pressure, time, temperature, and amount and concentration of sulphuric acid on the hydrolysis of sulphite pulp was studied by Simonsen.[5] Pressure, as obtained with chloroform, *e.g.*, is of no purpose without a correspondingly high temperature. In the tables given on page 344, the temperature corresponds with the various steam pressures.

Simonsen[6] concluded that from the standpoint of economy of operation the most suitable conditions for hydrolysis were: one part of cellulose and six parts of 0.5 per cent sulphuric acid heated for 1.5 hours at a pressure of 10 atmospheres. The yield of reducing sugars was 41 per cent. The yield of sugar is influenced by two principal factors, the speed of sugar formation and the speed of destruction of the sugar. It has been found

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[1] E. C. Sherrard and W. H. Gauger, *J. Ind. Eng. Chem.*, **15** (1923), 1164.

[2] H. Ost and L. Wilkening, *Chem. Ztg.*, **34** (1910), 461.

[3] H. Mühlmeister, *l.c.*, 38.

[4] J. Neuman, *l.c.*, 40.

[5] E. Simonsen, *Z. angew. Chem.*, **11** (1898), 219–228.

[6] E. Simonsen, *l.c.*, 223.

INFLUENCE OF PRESSURE AND CONCENTRATION OF ACID

(40 Grams Cellulose and 1080 Cubic Centimeters of Dilute H_2SO_4. Time 4 Hours)

Pressure, atmospheres	Concentration of acid, per cent			
	0.15 per cent	0.30 per cent	0.45 per cent	0.6 per cent
	Yield of sugar based on cellulose			
1.3	....	2.5	2.7	3.1
2.1	....	6.6	8.6	10.6
2.7	....	9.3	11.3	12.6
4.0	....	16.4	....	20.3
6.0	21.5	28.0	30.7	43.9
8.0	30.5	38.4	45.0	33.3
9.0	....	43.1		
10.0	35.0	36.6	30.0	18.0
12.0	38.4			
14.0	20.0			

INFLUENCE OF AMOUNT OF ACID

(40 Grams Cellulose and 4.8 Grams H_2SO_4 in Following Amounts of Water. Time, 2 Hours; Pressure, 8 Atmospheres)

Water, grams	Concentration of acid, per cent	Yield of sugar based on cellulose, per cent
250	1.5	18.4
500	0.75	35.0
1,080	0.44	45.4
1,500	0.23	32.5

INFLUENCE OF TIME

(40 Grams Cellulose and 250 Cubic Centimeters 0.5 Per Cent H_2SO_4. Pressure, 10 Atmospheres)

Time, minutes	Yield of sugar based on cellulose, per cent
15	20.1
37	37.3
45	38.2
60	39.0
75	40.0
90	42.7
120	35–40.9

preferable, therefore, in the case of wood to bring the pressure to 7.5 atmospheres as rapidly as possible and then relieve it.

Hydrolysis of cotton with sulphurous acid by the Classen process gave only 6.4 per cent of glucose.[1]

Cellulose, on exposure to the vapors of hydrochloric acid, is partially hydrolyzed to glucose. Air-dry cotton, after exposure for 1 week, gave 10.6 per cent of glucose, and after 2 weeks' exposure, 18.0 per cent.[2] The insoluble residue from the latter experiment, on hydrolysis with 0.5 per cent sulphuric acid at 175° for 30 minutes, gave 40 per cent of glucose, *i.e.*, 32 per cent based on the original cellulose. This shows that, contrary to the statements of others, Girard's hydrocellulose shows no peculiar resistance to hydrolysis.

Glucose,[3] identified through the osazone, is also formed in the preparation of hydrocellulose by treating cotton with dilute sulphuric acid, drying, and heating at 70°.

Sugars and Ethyl Alcohol from Wood.—Processes for the production of fermentable sugars from wood involve the use of: (1) dilute acids at high temperatures; (2) concentrated acids at low temperatures. Neither class has proved to be an unqualified success. The yield of fermentable sugars with dilute acids is insufficient to give a financially comfortable margin of safety, except under special circumstances. Concentrated acids give a high yield of sugars, but the recovery of the acids, which is necessary for economical operation, is beset with many engineering difficulties and requires a high plant investment.

Saccharification with Dilute Acids.—The hydrolysis of cellulose to glucose, though discovered in 1819, received scant attention until the middle of the century, when numerous papers of an industrial and scientific nature were published. Melsens[4] appears to have first hydrolyzed wood in an autoclave with dilute acid. He used concentrations of sulphuric acid of 3 to 10 per cent, and temperatures up to 200°. Payen[5] proposed to treat wood with dilute hydrochloric acid to obtain pulp, sugars being a by-product. Experiments by Thorn[1] gave 18 to 25 per cent of sugars. Zetterlund[2] heated wood with dilute hydrochloric acid at a pressure of 0.12 kilogram per square centimeter and obtained 19.7 per cent of sugars which were fermented to alcohol. He thought that hardwoods gave the best results.

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[1] J. Neuman, *l.c.*, 48.

[2] J. Neuman, *l.c.*, 66.

[3] W. Netthofel, "Beiträge zur Kenntnis der Zellulose," Diss. Berlin (1914), p. 36.

[4] G. F. Melsens, *Dinglers polytech. J.*, **138** (1855), 426–429.

[5] A. Payen, *Compt. rend.*, **64** (1867), 1167–1174.

The first systematic investigation was made by Simonsen,[3] who studied the effect of time, temperature, and concentration of acid. He heated 100 grams of sawdust with 500 cubic centimeters of sulphuric acid and obtained the following yields of sugar:

Effect of strength of acid (1 hour; 10 atmospheres)		Effect of pressure (temperature) (1 hour; 0.5 per cent acid)		Effect of time (9 atmospheres; 0.5 per cent acid)	
Strength of acid, per cent	Yield of sugar, per cent	Pressure, atmospheres	Yield of sugar, per cent	Time, minutes	Yield of sugar, per cent
0.30	18.4	8	18.2	7.5	22.2
0.58	19.6	9	19.6	15	22.5
0.75	19.2	10	19.6	30	20.8
1.00	19.6	11	19.2	60	19.6
1.50	5.0	12	15.2	90	16.6

He concluded that optimum conditions for saccharification were: 0.5 per cent acid; 9 atmospheres' pressure; 15 minutes' heating; and a ratio of dilute acid to wood of 5:1. The ratio could be reduced to 2.5:1 with hydrochloric acid, without decreasing the yield. Cooking of the residual wood gave 13 per cent additional sugar, a yield which did not justify recooking. Fermentations made on a semicommercial scale gave 2 to 6 per cent of alcohol, based on the dry wood.

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[1] W. Thorn, *Dinglers polytech. J.*, **210** (1873), 37–39.

[2] C. G. Zetterlund, *Wagner's Jahresber.*, **18** (1872), 597.

[3] E. Simonsen, *Biedermann's Zentr.*, **25** (1896), 47–50; *Z. angew. Chem.*, **9** (1898), 195–196, 219–228, 962–966, 1007–1012; U. S. P. 607091 (1898).

Reiferscheidt[1] and Körner[2] repeated Simonsen's work and likewise obtained 6 per cent of alcohol. Neuman[3] concluded that optimum conditions were 0.5 per cent acid, a temperature of 175°, and a reaction period of 30 minutes. A ratio of acid to wood of 3:1 was as favorable as 20:1. He obtained about 20 per cent of sugar. It was possible to obtain 44 per cent of sugar, or 16.6 per cent of alcohol, by hydrolyzing the wood several times.

Voerkelius[4] used sulphuric acid of a concentration of 0.2 to 2.0 per cent, at temperatures of 120 to 180°, and obtained uniformly about 25 per cent of sugar, or 8.6 per cent of alcohol.

The use of suphur dioxide was patented by Classen.[5] Among numerous defects that prevented the success of the process, the most important were the large amount of acid required and the long conversion time (4 to 6 hours). It was found that the more rapidly the contents of the digester could be brought to the required temperature, the shorter was the time required to obtain a maximum yield of sugar.[6] The conversion period was reduced to 45 minutes by the process of Ewen and Tomlinson,[7] in which live steam and sulphur dioxide were introduced directly into the digester. Sulphur dioxide was subsequently abandoned and dilute sulphuric acid substituted.[8] The operation of the process in a plant at Georgetown, S. C., has been described by von Demuth[9] and Foth.[10]

A distinct contribution to the art was made by Cohoe.[11] He heated the sawdust with live steam in such a manner that the amount of water present did not exceed 50 per cent of the weight of the sawdust, and when the gage pressure reached 50 pounds, hydrochloric acid was introduced. In 3 to 4 minutes, a maximum yield of 20 per cent of sugars was obtained. This "dry cook" has been generally adopted. The preliminary steaming of hardwoods gave 1 to 2 per cent of acetic acid.

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[1] Reiferscheidt, *Z. angew. Chem.*, **18** (1905), 44–48.

[2] T. Körner, "Zur Frage der Bildung von Alkohol aus Cellulose und cellulosehaltigen Stoffen," Diss. Dresden (1907); *Z. angew. Chem.*, **21** (1908), 2353–2359.

[3] J. Neuman, "Kritische Studien über Hydrolyse der Cellulose und des Holzes," Diss. Dresden (1910), 80 pp.

[4] G. A. Voerkelius, *Wochbl. Papierfabr.*, **42** (1911), 852–855.

[5] A. Classen, G. P. 118540 (1899); 130980 (1901).

[6] R. F. Ruttan, *J. Soc. Chem. Ind.*, **28** (1909), 1290–1294.

[7] M. F. Ewen and G. H. Tomlinson, U. S. P. 763472 (1904).

[8] M. F. Ewen and G. H. Tomlinson, U. S. P. 938308 (1909).

[9] R. von Demuth, *Z. angew. Chem.*, **26** (1913), 786–792.

[10] G. Foth, *Chem. Ztg.*, **37** (1913), 1221–1222, 1297–1298.

[11] W. P. Cohoe, *J. Soc. Chem. Ind.*, **31** (1912), 513–515; U. S. P. 985725 and 985726 (1911).

Ungar[1] studied the saccharification of wood with both concentrated and dilute acids, but obtained yields no higher than his predecessors. Hägglund[2] used concentrations of sulphuric acid of 0.25 to 1.5 per cent. He found that the best conditions were a temperature of 175°, and a ratio of wood to acid of 1:3. The highest yield, 20.8 per cent of sugar, or 87 liters of pure alcohol per long ton, was obtained with a 0.7 per cent acid and a conversion period of 30 minutes.

The most extensive investigation involving the use of dilute acids has been made by Kressmann.[3] The optimum conditions for coniferous woods were:

1. The temperature and pressure should not exceed 7.5 atmospheres.
2. This temperature and pressure should be reached as soon as technically possible, that is, in 15 to 20 minutes.
3. The digester should be held at the above temperature and pressure for 15 to 20 minutes.
4. The ratio of water to dry wood should be about 1.25:1.0.
5. The ratio of sulphuric acid (100 per cent) to dry wood should be from 1.8 to 2.5 to 100.
6. At the end of the cooking period, the digester should be blown as quickly as possible.

Under the above conditions, a yield of 25 gallons of 190-proof alcohol per dry ton of wood can be obtained, allowance being made for 2 to 5 per cent loss in distillation. Broad-leaved trees give only one-half as much fermentable sugars as do conifers.

Kressmann used concentrations of sulphuric acid up to 5 per cent of the weight of the wood. More concentrated acids will give more sugar, but not enough to justify the increased cost of the acid. Purvis[1] heated 25 grams of sawdust, 300 cubic centimeters of water, and 50 cubic centimeters of 85 per cent sulphuric acid, just below the boiling point, with constant stirring, for 5.25 hours. He obtained 39 per cent of sugars.

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[1] E. Ungar, Diss. Budapest (1916).

[2] E. Hägglund, *J. prakt. Chem.*, **91** (1915), 358–364.

[3] F. W. Kressmann, "The Manufacture of Ethyl Alcohol from Wood Waste," *U. S. Dept. Agr. Bull.*, **983** (1922), 100 pp.; *J. Ind. Eng. Chem.*, **6** (1914), 625–630; **7** (1915), 920–923; *Met. Chem. Eng.*, **15** (1916), 78–82.

A high yield of reducing sugars does not necessarily mean a high yield of alcohol, so that the sugars should always be fermented. Sherrard and Gauger[2] have used sulphuric acid up to 10 per cent of the weight of the wood. With 7.5 per cent of acid, at a pressure of 120 pounds for 15 minutes, they obtained only 23.6 per cent of reducing sugars, but the yield of alcohol was very high, namely, 29 gallons of 190-proof alcohol per ton of wood.

The actual yields of alcohol in plant operations have always fallen far below those obtained on a semicommercial scale. Tomlinson[3] states that the goal to be aimed at is 20 to 22 per cent of fermentable sugars or 35 gallons of alcohol per ton. The Georgetown plant is stated to have attained a yield of 19 gallons. Trial operations at the plant at Fullerton, La., in 1913, were exceedingly disappointing,[4] but during the war the yield was brought up to 15 gallons. There is every reason to believe that a properly constructed plant would produce 20 gallons of 95 per cent alcohol per ton of dry wood.[5]

Attempts have been made to increase the yield of sugars by the use of modified celluloses. Ekström[6] dissolved cellulose in 70 per cent sulphuric acid and after a few minutes precipitated it as an *acid cellulose* by the addition of water. The modified cellulose was not affected by dilute acids at atmospheric pressure, but was converted entirely into glucose at higher pressures. The acid cellulose was converted to soluble cellulose by triturating and heating it with one-fourth to one-half of its weight of 70 to 77 per cent sulphuric acid, at a temperature of about 80°;

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[1] J. E. Purvis, *Proc. Cambridge Phil. Soc.*, **19** (1919), 259–260.

[2] E. C. Sherrard and W. H. Gauger, *J. Ind. Eng. Chem.*, **15** (1923), 1165.

[3] G. H. Tomlinson, "Manufacture of Ethyl Alcohol from Wood Waste," Hon. Adv. Council for Sci. Ind. Res., Canada, *Bull.* **7** (1919), 9 pp.

[4] G. H. Tomlinson, *J. Ind. Eng. Chem.*, **10** (1918), 859–861.

[5] E. C. Sherrard, *Chem. Age*, **29** (1921), 76–79.

[6] G. Ekström, G. P. 193112 (1906).

it was then saccharified by diluting with water and boiling at atmospheric pressure for 0.5 to 1.0 hour.[1] Another method involved treating wood with sulphuric acid and sodium sulphate to produce *amyloid*, which was subsequently hydrolyzed with dilute acids.[2]

Schwalbe[3] proposes to treat wood containing less than 50 per cent of water with gaseous acids, such as sulphur dioxide and hydrogen chloride, until it swells but does not dissolve. The wood is then saccharified by heating with dilute acids. A nearly theoretical yield of sugars is claimed.

Gelatinization or swelling by means of acids, alkalis, and salts facilitates hydrolysis due to greater surface exposure; mechanical gelatinization is without effect. The formation of hydrocellulose should be avoided. The fact that cellulose can be only partially converted into glucose by means of dilute acids at atmospheric or higher pressures, and that the residue is more resistant to hydrolysis than the original, has never been satisfactorily explained; this phase of the subject has been discussed in the section on hydrocellulose. The data are conflicting and more work is needed. Neither the "reversion" hypothesis or that of a "skin effect," wherein the layer of hydrocellulose resists penetration by the acid, is fully acceptable. The saccharification of cotton is influenced but little by the presence of added glucose.

Much work has been done to increase the amount of sugar by the addition of catalysts other than the main acid. Gentzen and Roth[4] used ozone and claimed a yield of 34 per cent of glucose. Körner[5] found that potassium dichromate and potassium persulphate decreased the yield of alcohol; however, when a 2 per cent solution of hydrogen peroxide was used in place of water for dissolving the sulphuric acid, the yield of alcohol was nearly doubled, wood giving 9.0 to 10.7 per cent. Treatment of wood with ozone before hydrolysis decreased the yield.

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[1] G. Ekström, G. P. 207354 (1907).

[2] M. Mendelsohn and E. Frankl, G. P. 220634 (1908).

[3] C. G. Schwalbe, G. P. 305690 (1916); *Zellstoff u. Papier*, **4** (1924), 115–117.

[4] R. Gentzen and L. Roth, G. P. 745675 (1903).

[5] T. Körner, *l.c.*

Krull[1] treated wood with ozone, atmospheric oxygen at 150 to 170° for 2 to 6 hours, oxygen in presence of ammonia, chlorine at 20 to 40°, bleaching powder, nitric acid, nitrogen trioxide, alkalis, and water under pressure, then hydrolyzed with concentrated sulphuric acid. In every case the treatment reduced the yield of alcohol.

According to Classen,[2] the presence of a small amount of an acid or salt, differing from the main acid, decidedly increases the yield of sugar; thus if sulphuric acid is used, a small amount of hydrochloric or sulphurous acid should be added. Metals or oxides, particularly of the iron group, may also be used.

Kressmann[3] used mixtures of chemicals reacting according to the following equations:

1. $H_2SO_4 + NaCl = NaHSO_4 + HCl.$
2. $H_2SO_4 + 2NaCL = Na_2SO_4 + 2HCl.$
3. $2KClO_3 + H_2SO_4 + 10HCl = K_2SO_4 + 6H_2O + 6Cl_2.$
4. $2KClO_3 + H_2SO_4 = K_2SO_4 + 2HClO_3.$

It is improbable that in any case the reactions as given above proceeded to completion, but it is of interest that the yield of reducing sugars was practically the same (about 20 per cent) in each. Ferrous sulphate added to sulphuric acid was without effect. Niter cake alone or mixed with sulphuric acid reduced the yield of alcohol 20 to 25 per cent. Phosphoric acid gave only 15.7 gallons of alcohol per ton. Moore[4] proposes to hydrolyze wood with phosphoric acid and ferment the sugars without previous neutralization.

The use of manganese and magnesium chlorides in conjunction with hydrochloric acid has been protected.[5] Pink[6] claims a yield of 62 per cent of sugars by treating wood with alkalis, then hydrolyzing with dilute hydrochloric acid in the presence of chloracetic acid. Another method involves boiling the wood with formaldehyde under pressure previous to hydrolysis with acids.[7]

[1] H. Krull, "Versuche über Verzuckerung von Cellulose," Diss. Danzig (1916).

[2] A. Classen, G. P. 351681 (1917); E. P. 142480 (1920).

[3] F. W. Kressmann, *l.c.*, 54.

[4] H. K. Moore, U. S. P. 1323540 (1919).

[5] G. P. 359866 (1917).

[6] L. Pink, G. P. 362232 (1917).

[7] L. Pink, G. P. 362233 (1917).

The effect of a large number of chemicals, including inorganic acids, salts, and aromatic sulphonic acids, has been investigated by Sherrard and Gauger.[1] The additions usually caused a decrease in the yield of alcohol, while in no case was the yield sufficiently increased to warrant a change from the regular procedure.

Source of Ethyl Alcohol.—Körner[2] suggested that the yield of fermentable sugars was dependent on the cellulose content of the raw material. Gallagher and Pearl[3] asserted that the fermentable sugar was derived equally from the lignin and cellulose, the wood being attacked as a chemical entity, lignocellulose. The latter view is certainly erroneous. The alcohol is derived almost entirely from glucose and mannose, of which sugars mannose is the most important. The influence of the mannan of conifers was long overlooked.[4] The comparative absence of mannan in hardwoods, and the presence of large amounts of pentosans, explain the lower yield of alcohol from these woods. The differences in yield between species will be noted in the table below.

Western larch (*Larix occidentalis*) is of special interest, since it contains 8 to 17 per cent of galactan. At the time of its discovery, difficulty was encountered in fermenting galactose; about 40 per cent of alcohol was obtained with *Saccharomyces carlsbad* I.[5] Kressmann[6] obtained 30 per cent of reducing sugars on hydrolyzing the wood, but only 38 per cent was fermented with *S. cervisiœ,* the galactose remaining intact. Sherrard,[7] using the same yeast, was able to obtain very efficient fermentations by keeping the initial acidity[8] below 5° and the temperature between 85 and 90°F.; the conditions must be carefully observed. Autolyzed yeast sufficient to produce a 2 per cent solution was used as a nutrient. When the water-soluble portion of the wood and the residue were hydrolyzed separately, 40 gallons of 95 per cent alcohol were obtained per ton. This is the largest yield of alcohol that has been obtained from any

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[1] E. C. Sherrard and W. H. Gauger, *J. Ind. Eng. Chem.*, **15** (1923), 63, 1164.

[2] T. Körner, *l.c.*

[3] F. E. Gallagher and I. L. Pearl, *Eighth Int. Cong. Appl. Chem.*, N. Y., **13** (1912), 147–149.

[4] A. W. Schorger, *J. Ind. Eng. Chem.*, **9** (1917), 748.

[5] A. W. Schorger and D. F. Smith, *J. Ind. Eng. Chem.*, **8** (1916), 484.

[6] F. W. Kressmann, *J. Ind. Eng. Chem.*, **7** (1915), 920.

[7] E. C. Sherrard, *J. Ind. Eng. Chem.*, **14** (1922), 948; U. S. P. 1454521 (1923).

[8] In titrating 10 cubic centimeters of sugar solution, 1 cubic centimeter of $0.1N$ sodium hydroxide is equal to 1° of acidity.

YIELDS OF ALCOHOL FROM VARIOUS SPECIES OF WOODS[1]

Species	Total reducing sugars, per cent	Per cent of total reducing sugars		Alcohol yields	
		Fermentable	Unfermentable	Per cent of wood	Gallons 190 proof per ton
Conifers					
Western white pine	21.00	74.49	25.51	7.762	23.43
Red spruce	20.48	74.16	25.84	7.565	22.84
Red spruce	22.06	72.67	27.33	7.956	24.01
White pine	20.02	75.67	24.33	7.437	22.46
Longleaf pine	23.06	73.32	26.68	8.282	24.90
Longleaf pine	23.25	72.49	27.51	8.330	25.16
Lodgepole pine	21.93	67.37	32.63	7.205	21.75
Norway pine	25.63	66.88	33.12	7.745	23.38
Western larch	29.72	37.89	62.11	4.977	15.03
Western larch	30.52	57.88	42.12	8.687	26.21
Western larch	26.21	54.69	45.31	6.934	20.93
Western hemlock	21.15	77.63	22.37	7.622	23.01
Sugar pine	18.03	72.55	27.45	6.276	18.93
Sugar pine	20.23	66.49	33.51	7.115	21.47
White spruce	23.61	71.44	28.56	8.537	25.78
Douglas fir	21.10	67.42	32.58	6.822	20.59
Douglas fir	21.13	75.16	24.84	7.934	23.95
Hardwoods					
Birch	20.53	46.29	53.71	4.288	12.95
Sugar maple	18.93	34.04	65.96	3.029	9.14
Silver maple	20.74	47.22	52.78	4.661	14.07
Beech	21.24	22.22	77.78	1.995	6.02
White oak	17.30	50.48	49.52	4.102	12.38
Red oak	18.38	30.40	69.59	2.675	8.07
Sycamore	18.30	38.86	61.14	3.205	9.67
Slippery elm	16.60	26.79	73.21	1.382	5.98
Red gum	20.42	38.81	61.19	3.658	11.03
Cottonwood	18.19	32.86	67.14	2.392	7.21

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[1] F. W. KRESSMANN, *l.c.*, 57–58.

wood by hydrolysis with dilute acid. The yield fell to 33 gallons when the wood was hydrolyzed directly.

Sherrard and Blanco[1] have quantitatively determined the sugars formed by pressure hydrolysis of white spruce. Glucose and mannose formed two-thirds of the total sugars. Fructose was not detected.

	Per Cent
Mannose	37.7
Glucose	29.3
Galactose	6.4
Xylose	13.3
Arabinose	5.4
Reducing volatile substances	7.9
Total	100.0

The change in the composition of the wood, due to hydrolysis, was as follows:

Wood	Acetic acid by hydrolysis	Methoxyl	Pentosans	Cellulose	Lignin	Ash
Original	1.32	4.75	10.76	58.33	29.19	0.26
Hydrolyzed	0.116	3.99	1.79	39.67	29.63	0.06

It is surprising that the lignin content did not increase on hydrolysis, since 32 per cent of the cellulose was lost.

Saccharification with Concentrated Acids.—Braconnot,[2] in 1819, found that wood could be dissolved in concentrated sulphuric acid and largely converted into glucose. Arnould[3] treated 100 parts of sawdust with 110 parts of concentrated sulphuric acid, let stand 12 hours, diluted, boiled, neutralized with chalk, and fermented the sugars with yeast.

Voerkelius[4] treated one part of wood with seven parts of 70 per cent sulphuric acid and obtained 67 per cent of sugars, of which 70 per cent was fermentable. The yield of alcohol was 24.8 per cent, indicating practically complete saccharification of the hexosans. Similar experiments were made by Hägglund,[1] who treated the wood with an equal weight of 70 per cent sulphuric acid. He obtained the following yields:

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[1] E. C. Sherrard and G. W. Blanco, *J. Ind. Eng. Chem.*, **15** (1923) 611–616.

[2] H. Braconnot, *Ann. chim. phys.*, [2] **12** (1819), 172.

[3] J. E. Arnould, *Compt. rend.*, **39** (1854), 807–808.

[4] G. A. Voerkelius, *Wochbl. Papierfabr.*, **42** (1911), 852.

Time, hours	Temperature	Sugar on dry wood, per cent	Alcohol per long ton, liters
24	18°	23.5	80
48	18	54.8	158
3	40	29.1	120
5	40	34.9	125
3	50	26.6	105
6	50	23.9	102
2	75	16.0	
4	75	14.0	

Attempts have been made to reduce the amount of acid. Classen[2] subjected a mixture of 1 part of wood and 0.75 part of sulphuric acid of 57°Bé. to great pressure, whereby the mass became warm; on diluting with 4 parts of water and boiling, 40 per cent of the wood was converted into sugars. Wohl[3] employs powerful agitation and pressure; in this way 1.5 parts of sulphuric or hydrochloric acid suffice for 1 part of wood.

Hydrochloric acid is used in two ways: the wood is treated with hydrochloric acid of a concentration of 40 per cent or above;[4] or moistened with water and saturated with hydrogen chloride gas. The latter procedure was patented in 1880 in both England and Germany.[5] Wohl[6] subsequently rediscovered the method, but his patent application in Germany had to be withdrawn in view of the prior art. Krull[7] moistened wood with three parts of water, saturated it with hydrogen chloride, and completed the hydrolysis in the usual way. He obtained the following yields of reducing sugars and alcohol:

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[1] E. Hägglund, *J. prakt. Chem.*, **91** (1915), 358; "Die Hydrolyse der Zellulose und des Holzes," Stuttgart (1915), 52 pp.

[2] A. Classen, G. P. 111868 (1899).

[3] A. Wohl, E. P. 146860 (1920).

[4] R. Willstätter and L. Zechmeister, *Ber.*, **46** (1913), 2401; L. Zechmeister, Diss. Zürich (1913).

[5] A. M. Clark, E. P. 268 (1880); E. S. Dauzivillé, G. P. 11836 (1880).

[6] A. Wohl, W. 39800 (1912).

[7] H. Krull, Diss. Danzig (1916), 51; A. Wohl and H. Krull, *Cellulosechemie*, **2** (1921), 1–7.

Substance	Sugar, per cent	Alcohol, per cent	Alcohol in per cent of theoretical amount obtainable from sugar
Ground wood pulp..........	62.59	15.48	50.0
Spruce wood................	60.95	18.00	60.8

Other methods involve treatment of the wood with an equal weight of 40 per cent hydrochloric acid, followed in a short time by saturation with hydrogen chloride. The excess acid is removed by suction, and saccharification completed by diluting with water and boiling.[1] Terrisse and Levy[2] treat the wood with two parts of 33 per cent acid and add hydrogen chloride until the concentration of the acid reaches 41 per cent. Kocher[3] claims that almost complete saccharification is obtained with a 40 per cent acid in 24 to 48 hours at the ordinary temperature, and in much less time by working under pressure at a temperature of 40 to 60°.

Vernet[4] describes the saccharification of wood with hydrochloric acid. The apparatus resembles a Herreshoff pyrites burner; the wood, treated with aqueous hydrochloric acid, is placed in thin layers in a series of trays, and stirred by rotating arms while hydrogen chloride gas is introduced. The excess acid is removed by heat and suction. All parts of the apparatus in contact with the acid are made of "prodorite," a special material which is resistant to hydrochloric acid up to a temperature of 120°. The yield of absolute alcohol is 250 liters per long ton of sawdust, or about 19 per cent by weight.

The recovery of the large amounts of acids is a serious problem. Benesch[5] proposes to use ether for extracting the concentrated sulphuric acid, in large part, after the first stage of the reaction.

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[1] Chem. Fabrik Rhenania, F. L. Schmidt, and G. A. Voerkelius, G. P. 304399 (1917).

[2] H. Terrisse and M. Levy, E. P. 143312 (1920).

[3] R. A. Kocher, E. P. 107219 (1916).

[4] G. Vernet, *Chimie & Industrie*, Special No. (May, 1923), 654–657.

[5] E. Benesch, G. P. 368399 (1920).

Sufficient acid remains to complete the hydrolysis by diluting the residue with water and heating. Budnikow and Solotarew[1] place the dilute sulphuric acid solution of the sugar in the cathode compartment of an electrolytic cell; the cathode is surrounded by a porous pot. On electrolysis, 91.5 per cent of the sulphuric acid is recovered in the anode compartment, with the consumption of 7.215 kilowatts per kilogram of acid. The power consumed is worth more than the acid recovered.

The most practical method of recovering hydrochloric acid appears to be by the use of a vacuum. According to Budnikow[2] and Sworykin, 98.74 per cent of the hydrochloric acid can be recovered as chlorine by electrolysis, using *platinum* electrodes. The sugar content of the solution surrounding the cathode is unchanged. It is claimed that a purer sugar solution is obtained in this way than by the use of dilute sulphuric acid, which is precipitated with calcium carbonate. An objection to the use of hydrochloric acid is the necessity of removing the chlorine ions, towards which yeast is intolerant;[3] this cannot be accomplished as economically as with sulphuric acid.

Products.—The ethyl alcohol obtained from wood is remarkably pure; it contains 0.5 per cent fusel oil, a trace of methyl alcohol, and no acetone.[4]

The hydrolysis of coniferous woods gives about 2.0 per cent of acetic and formic acids, of which acetic acid constitutes about 80 per cent.[5] Only about 10 per cent of each acid is obtained in relieving the pressure in the digester, so that the recovery would not pay. Pringsheim[6] prepared a stock food by treating wood with dry steam and gaseous hydrochloric acid (1.5 per cent) at a temperature of 120 to 140°. He obtained as by-products 6.04 per cent of acetic acid, 1.68 per cent of acetone, and 3.5 per cent of furfural.

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[1] P. P. Budnikow and P. W. Solotarew, *Chem. Zentr.*, **93**, IV (1922), 324; P. P. Budnikow, *Z. angew. Chem.*, **36** (1923), 326–328.

[2] P. P. Budnikow and A. I. Sworykin, *Z. angew. Chem.*, **35** (1922), 677.

[3] F. W. Kressmann, *l.c.*, 54.

[4] G. Foth, *Chem. Ztg.*, **37** (1913), 1298.

[5] F. W. Kressmann, *l.c.*, 48, 84.

[6] H. Pringsheim, *Cellulosechemie,* **2** (1921), 123–124.

Only qualitative tests appear to have been made for lævulinic acid in the hydrolyzate. Bente[1] boiled fir wood with 5 per cent sulphuric acid for 8 days and obtained a small amount of lævulinic acid. Noyer[2] has calculated that a long ton of sawdust could give 250 kilograms of lævulinic acid, which might serve as a raw material for synthetic rubber. The acid, on distillation with phosphorous trisulphide, gives mainly α-methylthiophene, which on reduction yields isoprene.

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[1] F. Bente, *Ber.*, **8** (1875), 416–418.

[2] G. Noyer, *Caoutchouc & gutta-percha*, **13** (1916), 8804–8805.

CHAPTER XI

THE ACTION OF VARIOUS REAGENTS ON WOOD

Wood is almost inert to water, except at high temperatures, and is dissolved with difficulty by all cellulose solvents. Bases attack the lignin preferentially, but at high temperatures the caustic alkalis convert both cellulose and lignin into aliphatic acids. Hot acids disintegrate wood by hydrolysis of the carbohydrates. Oxidizing agents attack lignin profoundly and convert the cellulose to oxycellulose. The decomposition of wood under atmospheric conditions is due to a slow oxidation.

Action of Heated Water.—Wood becomes soft and pliable when heated with water, and at sufficiently high temperatures undergoes hydrolysis. Tauss[1] heated wood with water at various pressures up to 20 atmospheres and found that maximum solubility was reached at 5 atmospheres. Repetition of cooking did not greatly increase the extract. A single cook at 10 atmospheres dissolved 13.68 per cent of birch, and 11.78 per cent of spruce; at 20 atmospheres, only 3.34 per cent of birch dissolved. None of the sugars formed were identified. Filter paper became gelatinous at a pressure of 20 atmospheres and dried to a hard mass. Schwalbe and Robinoff[2] have shown that pure cellulose

Solubility of Wood in Water at 5 Atmospheres' Pressure

Wood		Cook number			Total, per cent
		1, per cent	2, per cent	3, per cent	
Beech	Dry extract	21.60	4.00	1.25	26.75
	Sugar in extract	9.85	1.19	0.15	11.19
Spruce	Dry extract	15.40	3.07	0.71	19.18
	Sugar in extract	8.00	1.00	0.08	9.08

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[1] H. Tauss, *Dinglers polytech. J.*, **273** (1889), 276–285.

[2] C. G. Schwalbe and M. Robinoff, *Z. angew. Chem.*, **24** (1911), 256–258.

undergoes very slight change on being heated with water at pressures up to 20 atmospheres; a temperature of 150° should not be exceeded, however, as the decomposition becomes noticeable at this point.

Wood is converted into a carbonaceous mass resembling coal when heated with water at a temperature of 250°.[1]

The sugars produced by pressure hydrolysis were more carefully examined by Koch.[2] He used the wood of aspen (*Populus tremula*) and spruce (*Picea excelsa*) which had been purified by treatment in the cold with water, 5 per cent hydrochloric acid, water, 5 per cent ammonium hydroxide, and finally with 10 per cent sodium hydroxide to remove wood gum. The purification resulted in great loss; starting with 1 kilogram, 520 grams of aspen and 550 grams of spruce were obtained as a purified residue. Purified spruce, heated with water at 5 atmospheres' pressure (150°), gave a syrup containing:

	Per Cent
Lævulinic acid	7.8
Mannose	29.2
Glucose	23.9
Galactose	0
Fructose (Seliwanoff reaction)	Trace

No pentoses were detected, but the syrup gave 8.9 per cent furfural. The furfural-yielding substances were largely destroyed by evaporating the syrup at 100°. The survival of mannose in the purified wood is noteworthy.

Aspen gave mannose, galactose, glucose, and fructose (trace). Xylose and arabinose were not found. Celluloses prepared with Schulze's reagent were also tested. He concludes that, while mannose and galactose are formed from lignocelluloses, they originate from the lignin complex and not from the cellulose. Glucose is derived from the cellulose. Galactose and mannose are formed readily at low temperatures and destroyed at 185°. Fructose is formed only in traces, but there is more in spruce than in poplar. The presence of sugars other than glucose shows that the hemicelluloses had not been completely removed, in spite of the purification.

[1] S. Stein, *Chem. Zentr.*, **72,** II (1901), 950.

[2] W. Koch, "Verhalten von Lignocellulose beim Erhitzen mit Wasser unter Druck," Diss. Freiburg (1909), 39 pp.

The amount of sugar formed from a wood gel is somewhat lower than from normal wood.[1] In the following table, Norway pine was heated with water in an autoclave, held at the maximum pressure for 15 minutes, and the pressure released.

Cook number	Steam pressure, pounds	Sugars from	
		Normal wood, per cent	Gelatinized wood, per cent
1	75	2.93	1.11
2	125	6.50	4.79
3	200	9.03	8.55
4	250	7.53	6.48

In the manufacture of mechanical pulp, the longest and strongest fibers are prepared by the hot process. According to Kirchner,[2] the steam suddenly developed when the wood comes in contact with the stone exerts a softening action on the incrustants holding the fibers together, and they are burst apart. The brown color of steamed pulp is probably due to oxidation, since in the presence of reducing agents no coloration takes place.[3]

The solubility of lignin in water is very slight, though Potter[4] thought that both cold and hot water produced delignification of the xylem, since the extracts gave the lignin reaction. Spaulding[5] found that very slight delignification could be produced in thin sections of wood heated in an autoclave with water at 120°. The lignin of spring wood was more soluble than that of summer wood. An annual ring of *Pinus palustris,* boiled in water and stained with phloroglucinol, showed a red coloration of the summer wood, while the spring wood retained practically its natural color. Zeller,[6] using zinc chloriodine, was unable to observe any change in the lignification of autoclaved wood, though the aqueous extracts gave a faint pink with phloroglucinol.

[1] A. W. Schorger, *J. Ind. Eng. Chem.,* **15** (1923), 812.

[2] E. Kirchner, *Wochbl. Papierfabr.,* **41** (1910), 1995.

[3] C. G. Schwalbe, G. P. 203230 (1908).

[4] M. C. Potter, *Ann. Botany,* **18** (1904), 121.

[5] P. Spaulding, *Missouri Botan. Gardens,* **17** (1906), 41–58.

[6] S. M. Zeller, *Ann. Missouri Botan. Gardens,* **4** (1917), 93.

Wood steamed or boiled for mechanical pulp is stained *blue* by zinc chloriodine.[1] Wood loses 3 to 4 per cent of extractives by the boiling process, but only 0.1 to 0.2 per cent by steaming. Microscopic examination indicated a loosening of the bond between the tracheids of the summer wood.

Heating wood with water under pressure produces methyl alcohol,[2] and acetic and formic acids. Bergström[3] heated wood with water at a pressure of 6 atmospheres for 2 hours, and obtained the following amounts of acids:

Species	Acetic acid, per cent	Formic acid, per cent	Ratio of formic to acetic acid
Spruce	1.53 1.17	0.23 0.21	1:6.65 1:5.57
Pine	1.40 1.24	0.22 0.19	1:6.36 1:6.53
Birch	3.13	0.16	1:19.56

Steaming coniferous wood at 4 atmospheres' pressure for 8 hours gave a solution containing sugars, resin, tannin, furfural, salts, and organic acids.[4] No furfural is obtained by steaming at atmospheric pressure even in the presence of formic and acetic acids.[5] The formation of furfural was first noted by Williams.[6] He obtained 0.63 per cent of furfural by steaming wood at 100 pounds' pressure for 4 hours.

	Per cent
Acetic acid	0.213
Formic acid	0.32
Sugar	5.20

The steaming of 27 solid cubic meters of wood gave:[1]

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[1] F. A. Zacharias, *J. Soc. Chem. Ind.*, **31** (1912), 582.
[2] H. Bergström, *Papier-Fabr.*, **8** (1910), 506, 736.
[3] H. Bergström, *Papier-Fabr.*, **11** (1913), 305–306.
[4] E. Heuser, *Chem. Ztg.*, **38** (1914), 126–127.
[5] E. Heuser, *Z. angew. Chem.*, **27** (1914), 654–655.
[6] G. Williams, *Chem. News*, **26** (1872), 231.
[7] C. Franck, *Papier-Fabr.*, **17** (1919), 1019–1020.

	Kilograms
Amines (principally methylamine)	0.20
Acetone	0.14
Methyl alcohol	5.12
Furfural	8.80
Methylfurfural (?)	0.12
Volatile acids (principally acetic)	40.00
Sugars	80.00
Humus substances	147.00

Action of Cellulose Solvents.—Wood dissolves reluctantly in all cellulose solvents. Soon after the discovery of Schweizer's reagent, it was observed that wood was scarcely affected by it. The conclusion was accordingly drawn that the lignin must be chemically combined with the cellulose.[1] Webster[2] states that plant fibers without exception dissolve more or less rapidly in contact with metallic copper and strong ammonia; conflicting statements are due to the use of cuprammonium solutions of different activity.

Hoffmeister[3] found that by subjecting lignocelluloses to alternate treatment with hydrochloric or acetic acid, and ammonia, that incrustants were so modified that the cellulose could be completely dissolved with cuprammonium solution. According to Ungar,[4] wood consists of portions rich in cellulose and poor in lignin which are dissolved, and portions high in lignin which are not. Spruce wood after 13 extractions with cuprammonium solution gave a residue of 37 per cent. The methoxyl content of the soluble portions varied from 2.19 to 5.80 per cent, while the residue contained 9.03 per cent. Roughly, the soluble fractions contained 15 to 40 per cent of lignin, and the residue 60 per cent. Willstätter lignin dissolved to the extent of 3 per cent.

The difficulty in dissolving the cellulose is only partially due to the mechanical interference of the lignin. Birch wood was ground with cuprammonium solution in a ball mill for 72 hours, and the insoluble residue again treated with cuprammonium solution. The residue from the second treatment contained 34 per cent of lignin, 10 per cent of pentosans, and 56 per cent of cellulose.[1]

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[1] C. Cramer, *J. prakt. Chem.*, **73** (1858), 2; E. Fremy, *Compt. rend.*, **48** (1859), 277; J. Erdmann, *Ann. Suppl.*, **5** (1867), 224; G. Lange, *Z. physiol. Chem.*, **14** (1890), 19.

[2] C. S. Webster, *J. Chem. Soc.*, **43** (1883), 25.

[3] W. Hoffmeister, *Landw. Jahrb.*, **17** (1888), 261; **18** (1889), 773; *Landw. Vers.-Sta.*, **50** (1898), 359.

[4] E. Ungar, Diss. Budapest (1916), 84, 90, 102.

A solution of zinc chloride in twice its weight of concentrated hydrochloric acid is stated to generally dissolve jute and lignocellulose.[2] Ungar[3] heated spruce with a solution of 100 grams of zinc chloride in 55 cubic centimeters of water at 70 to 80°. Seven extractions gave an insoluble residue of 32 per cent. The reagent first demethylates, then hydrolyzes.

The solvent action on wood of thiocyanate solutions is very slight.[4]

The thiocarbonate reaction, applied to thin wood shavings, gave a product having none of the characteristic properties of viscose.[5] The wood of *Æschynomene aspera* swelled and became gelatinous, but only 20 to 30 per cent went into solution.[6] Less than 10 per cent of elder pith was made soluble.[7]

There is a progressive increase in the solubility of wood by the thiocarbonate reaction, beginning with wood flour and ending with gelatinized wood.[8] Wood ground in a ball mill with a mercerizing solution of sodium hydroxide, then treated with carbon bisulphide, showed the following solubilities:

	Per Cent
Aspen	81.80
White pine	69.85

The soluble portion precipitable by acid contained considerable lignin:

Precipitate from	Lignin, per cent	Pentosan, per cent	Pentosan-free cellulose (by difference), per cent
Aspen (*Populus tremuloides*)	11.70	10.93	77.37
White pine (*Pinus strobus*)	22.20	8.32	69.48

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[1] A. W. Schorger, *J. Ind. Eng. Chem.*, **16** (1924), 141.

[2] C. F. Cross and E. J. Bevan, *Chem. News*, **63** (1891), 66.

[3] E. Ungar, *l.c.*, 96.

[4] H. E. Williams, *J. Soc. Chem. Ind.*, **40** (1921), 221T.

[5] C. F. Cross, E. J. Bevan, and C. Beadle, *J. Chem. Soc.*, **67** (1895), 444.

[6] W. C. Hancock and O. W. Dahl, *Chem. News*, **72** (1895), 18.

[7] C. F. Cross and E. J. Bevan, "Researches" (1895–1900), p. 137.

[8] A. W. Schorger, unpublished results.

Wood that has been subjected to hydrolysis surrenders its cellulose readily and gives a thiocarbonate solution of low viscosity. The recovered cellulose contained:

	Per Cent
Pentosan	0.63
Lignin	1.04
"Cellulose"	98.33

Action of Bases.—Ammonia, for a weak base, has a high solvent action on wood, tannins, coloring matters, resins, lignin, pentosans, etc. being removed. According to Hoffmeister,[1] wood extracted with concentrated ammonia for several days no longer gives the lignin reaction. The residue from evaporation of the solvent smelled strongly of vanillin. Complete extraction of wood may take months.[2]

When yellow birch was ground in a ball mill with concentrated ammonia, 14.45 per cent of the wood dissolved [3] The solubility of wood passing a 100-mesh sieve, when digested in the cold with a 2 per cent solution of ammonia, NH_3, for 24 hours was:[4]

Species	Ammonia Extract, Per Cent
White pine	12.96
Sugar maple	8.44
Aspen	8.08
Yellow birch	7.06

The alkaline earths have little effect on wood. The use of alkalis for removing lignin to obtain wood pulp is treated on page 403.

Schleiden[5] observed that when raspings of Scotch pine were treated with excess of a solution of potassium hydroxide and heated until a crust formed, the residue stained a bluish black with iodine. Long boiling with water destroyed this property.

Tauss[6] heated cellulose (Swedish filter paper), spruce wood, and beech wood with various strengths of sodium hydroxide at different pressures. Spruce, after three successive boilings with 8 per cent sodium hydroxide at atmospheric pressure, lost 49.19

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[1] W. Hoffmeister, *Landw. Jahrb.*, **17** (1888), 261.

[2] W. Hoffmeister, *Landw. Vers.-Sta.*, **48** (1897), 409.

[3] A. W. Schorger, *J. Ind. Eng. Chem.*, **16** (1924), 141.

[4] A. W. Schorger, *J. Ind. Eng. Chem.*, **15** (1923), 812.

[5] M. J. Schleiden, *Ann.*, **42** (1842), 300.

[6] H. Tauss, *Dinglers polytech. J.*, **276** (1890), 411–428.

per cent of its weight, and beech 54.68 per cent. The losses obtained by a single treatment with alkali for 3 hours, are given below:

NaOH solution, per cent	Pressure, atmospheres	Loss in weight of		
		Cellulose, per cent	Spruce, per cent	Birch, per cent
3	0	12.07	28.37	30.25
3	5	15.36	50.96	55.66
3	10	20.28	70.31	65.59
8	5	.....	56.91	64.36
8	10	.....	74.32	70.66
14	0	21.88	35.45	46.43
14	5	77.33	97.13	91.48

With increase in temperature and strength of alkali, the wood approaches complete solubility.

Formation of Oxalic Acid.—At high temperatures, wood in the presence of the caustic alkalis is oxidized to acetic, formic, and oxalic acids, the latter predominating. Beyond solution of the lignin, wood does not undergo much change at temperatures below 180° in the absence of air. Hoppe-Seyler[1] recognized no change in filter paper heated with a strong solution of potassium hydroxide at 200°. At a temperature of 240°, he obtained catechol, protocatechuic, oxalic, formic, and acetic acids. The gas consisted mainly of hydrogen, with some methane. Lange's[2] method for determining cellulose is based on heating wood with a strong solution of the caustic alkalis at a temperature of 140 to 180° for an hour; the incrusting substances pass into solution, leaving a residue (51 to 55 per cent) of modified cellulose.

Gay-Lussac,[3] who discovered the formation of oxalic acid by fusing carbohydrates with alkalis, stated that sodium hydroxide could be used as well as potassium hydroxide. Possoz[4] found that equal parts of potassium and sodium hydroxide could be used, but that sodium hydroxide could not be used alone. He

[1] F. Hoppe-Seyler, *Z. physiol. Chem.*, **13** (1889), 77, 79.

[2] G. Lange, *Z. physiol. Chem.*, **14** (1890), 283–288.

[3] J. L. Gay-Lussac, *Ann. chim. phys.*, [2] **41** (1829), 398–402.

[4] L. Possoz, *Compt. rend.* **47** (1858), 207, 648.

obtained 70 parts of oxalic acid by fusing 100 parts of sawdust and 300 parts of potassium hydroxide. Dale[1] reduced the method to commercial practice.

The reaction was studied by Thorn,[2] who found that sodium hydroxide could be used alone but that the yield of oxalic acid was low. He used a mixture of 50 grams of sawdust and 100 grams of alkali, in the form of a solution of 42°Bé., and heated it in layers 1 centimeter thick on an iron plate for 1.5 hours. The most economical ratio of KOH:NaOH was 40:60. The use of air preheated to 100 to 120°, though it accelerated the reaction, and the use of manganese dioxide did not increase the yield. Coniferous woods gave 94.7 per cent oxalic acid and hardwoods 83.4 to 93.1 per cent.

Yields of Oxalic Acid by Alkaline Fusion of Sawdust

Ratio KOH: NaOH	Temperature	Oxalic acid, $C_2H_2O_4.2H_2O$, per cent
0: 100	200–220°	33.14
10: 90	230	58.36
20: 80	240–250	74.76
30: 70	240–250	76.77
40: 60	240–250	80.57
60: 40	240–250	80.08
80: 20	245	81.24
100: 0	240–250	81.23

Preen[3] fused one part of sawdust with two parts of sodium hydroxide and obtained 35.2 per cent of oxalic acid at 200°, and 30.0 per cent at 220°. Fusion with four parts of alkali at 240° increased the yield to 41 per cent. Various methods involving technic and the use of catalysts have been protected.[4]

[1] J. Dale, E. P. 2767 and 3031 (1856).

[2] W. Thorn, *Dinglers polytech. J.*, **210** (1873), 24–39.

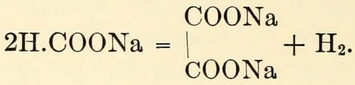
[3] F. H. E. Preen, *Chem. Age*, **32** (1924), 72.

[4] J. Dale, E. P. 2137 (1872); Capitaine and von Hertling, G. P. 84230 (1895); G. F. Zacher, E. P. 2308 (1897); H. Plater-Syberg, E. P. 23682 (1893); Effront, F. P. 373157 (1906); A. Deiss and C. J. Fournier, F. P. 406722 (1909); C. Ellis, U. S. P. 1001937 (1911); H. O. Chute and K. P. McElroy, U. S. P. 1002034 (1911); L. W. Andrews, 1018092 (1912); 1065577 (1913); F. Mori and J. Maeda, Jap. P. 37100 (1920), C. A., **16** (1922), 105.

Droste[1] uses an alkaline permanganate solution, while Hofmann[2] heats wood with nitrates or chlorates in the presence of magnesium salts.

The alkaline fusion process has been largely supplanted by a synthetic method. Carbon monoxide is heated with a solution of sodium hydroxide to obtain sodium formate, which on heating to a temperature of 350 to 400° decomposes into hydrogen and oxalic acid.

$$\mathrm{CO + NaOH = H.COONa.}$$



$$\mathrm{2H.COONa} = \begin{array}{c}\mathrm{COONa}\\ | \\ \mathrm{COONa}\end{array} + \mathrm{H_2}.$$

Thorn[3] was of the opinion that the oxalic acid was formed almost entirely from the carbohydrates. Von Hedenström[4] obtained 124 per cent of oxalic acid from cotton and 122 per cent from oak sawdust, using four parts of potassium hydroxide and a temperature of 280°. Preliminary extraction of the wood with 10 per cent potassium hydroxide reduced the yield of oxalic acid, from which it was concluded that some of the oxalic acid was derived from the lignin. Lignin does give oxalic acid, but under the usual conditions of fusion none is obtained.[5]

The formation of acetic acid by the fusion of wood with potassium hydroxide was observed by Erdmann.[6] The acetic acid arises partly by saponification of acetyl groups, but mainly by oxidation. Better yields are obtained with potassium hydroxide than with sodium hydroxide, and with three parts of alkali than with one.[7] The following yields were obtained with three parts of potassium hydroxide:

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[1] A. Droste, G. P. 199583 (1906).

[2] K. Hofmann, G. P. 277733 (1913).

[3] W. Thorn, *l.c.*

[4] A. von Hedenström, *Chem. Ztg.*, **35** (1911), 853–854.

[5] E. Heuser, *Papier-Fabr. Fest u. Auslandsheft*, **19** (1921), 75; E. Heuser and A. Winsvold, *Cellulosechemie*, **2** (1921), 113.

[6] J. Erdmann, *Ann. Suppl.*, **5** (1867), 228.

[7] C. F. Cross, E. J. Bevan, and J. F. V. Isaac, *J. Soc. Chem. Ind.*, **11** (1892), 966–969.

	At 150° acetic acid, per cent	At 200 to 250° acetic acid, per cent
Cane sugar	46.0	33
Hydrocellulose (from cotton)	19.5	29
Jute	15.0	37
Pine wood	18.0	28

The optimum conditions for the formation of formic and acetic acids were fully investigated by Mahood and Cable.[1] At the lower temperatures, about equal parts of formic and acetic acids are obtained. At a temperature of 230°, the yield of acetic reaches a maximum of 19 per cent; the yield of oxalic acid is about 60 per cent. About 2.3 per cent of methyl alcohol is formed during the fusion.

Action of Acids.—The hydrolysis of wood for the production of fermentable sugars is treated in Chapter X. Wood impregnated with a dilute acid, such as sulphuric, and allowed to dry is converted into brittle hydrocellulose. Charring takes place at elevated temperatures. The same effect is obtained with salts which hydrolyze readily to form mineral acids.

Kolbe[2] states that salicylic acid is *destroyed* by wood; it disappears completely from a dilute solution (0.2 gram to the liter) and cannot be detected in the wood. The phenomenon is probably due to adsorption or condensation.

Wood and cellulose, when treated with concentrated nitric acid in the cold, swell and form a gel which Braconnot[3] termed xyloidin. Mulder[4] treated wood with fuming nitric acid; after 4 days, he obtained a gelatinous product which he considered to be pure cellulose. Sacc[5] heated spruce wood with nitric acid of sp. gr. 1.40 and obtained a gelatinous substance which he believed to be pectic acid, but which was in reality oxycellulose.[6]

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[1] S. A. Mahood and D. E. Cable, *J. Ind. Eng. Chem.*, **11** (1919), 651–655.

[2] H. Kolbe, *J. prakt. Chem.*, **21** (1880), 443; **22** (1880), 112.

[3] H. Braconnot, *Ann. chim. phys.*, [2] **52** (1833), 293.

[4] G. J. Mulder, *J. prakt. Chem.*, **39** (1846), 150–155.

[5] F. Sacc, *Ann. chim. phys.*, [3] **25** (1849), 218–230.

[6] J. B. Lindsey and B. Tollens, *Ann.*, **267** (1892), 366.

Organic Acids by Alkaline Fusion of Wood[1]
(Results in Per Cent—Ratio NaOH: Sawdust, 3:1)

Species	Time, hours	170°			200°			230°		
		Acetic	Formic	Oxalic	Acetic	Formic	Oxalic	Acetic	Formic	Oxalic
White oak (*Quercus alba*).	3	6.4	7.3	24.1	10.2	12.3	31.5	17.0	5.7	38.4
	6	8.4	9.8	....	13.6	7.7	55.3	17.6	2.3	33.3
	12	11.4	14.5	38.0	15.6	4.6	62.5	18.9	0.8	40.4
Maple (*Acer saccharum*)..	3	5.3	3.3	....	12.8	11.1	46.4	17.8	1.1	58.7
	6	8.1	7.7	....	15.7	5.9	59.3	18.1	2.3	46.4
	12	7.2	6.7	....	16.3	4.5	....	19.1	2.9	
Longleaf pine (*Pinus palustris*).	3	3.1	4.6	6.5	6.4	8.6	30.0	12.0	4.9	68.9
	6	8.4	12.0	37.2	14.4	2.3	70.0	14.0	1.8	69.3
	12	12.6	15.3	58.0	14.7	5.1	74.0	14.6	1.2	67.4

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[1] S. A. Mahood and D. E. Cable, *l.c.*

Cold strong nitric acid or hot dilute acid oxidizes wood rapidly, the lignin, especially, being attacked. Nitric acid of sp. gr. 1.35 to 1.40, when poured upon sawdust, gives off red fumes followed by a dense white smoke, then ignition.[1] Acid of sp. gr. 1.268 to 1.236 produces vapors but no flame.[2] It is not surprising that the practice of silver reclaimers of absorbing a solution of silver nitrate and nitric acid in sawdust has led to fires.[3]

Nitric acid,[4] and a mixture of nitric and sulphuric acids,[5] have been suggested for producing pulp from wood. Cross[6] used a 10 per cent solution of nitric acid at a temperature of 80°, and proposed the recovery of acetic and oxalic acids from the mother liquor. Hedén[7] claims the formation of picric acid, in addition.

Lifschütz[8] heated pine wood for 14 to 16 hours, at a temperature of 45 to 60°, with a solution containing 32 per cent of sulphuric acid and 18 to 20 per cent of nitric acid; after washing with sodium hydroxide, about 40 per cent of cellulose was obtained. The yield of oxalic acid was 29 to 30 per cent. The gases evolved could be oxidized to nitric acid for reuse.

According to Cross and Bevan,[9] the reaction is not one of simple oxidation. The nitrous acid reacts with methylene groups in the lignin to give oximes which are subsequently oxidized:

$$1.\ X.CH_2 + O.NOH = X.C{:}NOH + H_2O.$$

$$2.\ X.C{:}NOH + O.NOH = X.CO + N_2O + H_2O.$$

The formation of considerable quantities of hydrocyanic acid strengthens this view. Nitric acid of a concentration of 4 to 7 per cent, at a temperature of 60°, converts the lignin into an acid derivative poor in nitrogen, having the formula $C_{25}H_{39}NO_{25}$ and forming salts of the formula $C_{25}H_{31}NO_{25}M.''_4$ Oxidation with dilute nitric acid may be prevented by the addition of urea, which destroys the nitrous acid; the nitric acid then has only a hydrolytic action and behaves like sulphuric or hydrochloric acid.

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[1] L. Archbutt, *J. Soc. Chem. Ind.*, **15** (1896), 84–85.

[2] R. Hass, *Chem. Ind.*, **8** (1885) 173; *Analyst*, **6** (1881), 231.

[3] W. L. Wedger, *J. Ind. Eng. Chem.*, **11** (1919), 894.

[4] C. H. Barne and C. M. Blondel, *Dinglers polytech. J.*, **164** (1862), 464; **172** (1864), 238.

[5] J. Lifschütz, E. P. 1824 (1891).

[6] C. F. Cross, E. P. 409 (1894).

[7] J. E. Hedén, G. P. 212838 (1908).

[8] J. Lifschütz, *Ber.*, **24** (1891), 1186–1192.

[9] C. F. Cross and E. J. Bevan, *Ber.*, **24** (1891), 1772–1776.

Baly and Chorley[1] heated beech wood with a 10 per cent solution of nitric acid on the water bath for 4 hours. The gas evolved had the following composition:

	N	N_2O	NO	NO_2	HCN	CO_2	CO
Per cent.......	18.3	9.4	9.3	33.2	8.3	17.2	4.3

The products of oxidation were:

	Per Cent
Fibrous residue (nearly pure cellulose)	48.00
Volatile acids (mainly acetic, and calculated as such)	11.80
Oxalic acid	3.84
Soluble incrusting substances	26.16

Spruce wood gave only 3 to 4 per cent of volatile acids, as it represents a different type of lignification.

Dry wood will take up 10 per cent of its weight of dry hydrogen chloride, in comparison with less than 1 per cent for cotton and hydrocellulose.[2]

Action of Salts.—Little information is available on the action of salts on wood, except in cases where they have been used for wood preservation. Some salts appear to be adsorbed in small amounts.[3] The assumed chemical combination with wood of a salt such as zinc chloride is usually due to the deposition of an insoluble basic salt.

Boucherie[4] claimed that iron acetate exerted a peculiar action on wood, not only preserving it against decay, but rendering it very hard and dense. He proposed treating wood with hygroscopic salts to preserve flexibility and elasticity.

It is an ancient observation that when iron nails are driven into wood exposed to air and moisture the surrounding wood is rapidly destroyed by oxidation.[5] The iron oxide may cause catalytic oxidation by atmospheric oxidation, or by hydrogen peroxide.

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[1] E. C. Baly and J. C. Chorley, *Ber.*, **28** (1895), 922–927.

[2] E. Ungar, Diss. Budapest (1916), 58.

[3] P. Casparis, C. A., **15** (1921), 1333. Original papers not available.

[4] A. Boucherie, *Ann. chim. phys.*, **274** (1840), 145.

[5] K. Micksch, *Chem. Zentr.*, **91**, IV (1920), 554.

König[1] states that copper sulphate can be readily washed out of hardwoods, but that in coniferous woods it appears to combine with the resin. Copper salts have a highly protective action against decay. In a copper mine in Portugal, dating from the time of the Romans under Nerva, Payen[2] records the finding of a wheel which was in a good state of preservation. The wood contained about 1 per cent of copper sulphate and 3 per cent of basic iron sulphate.

Mercuric chloride is adsorbed from its solutions.[3] When wood is immersed in a solution of zinc hydrogen fluoride, $ZnFl_2.2HF$, containing free hydrofluoric acid, the compound is adsorbed as such; if the solution is forced into the wood by pressure an excess of fluorine over zinc is taken up.[4] In the case of a mixture of zinc chloride and sodium fluoride there is adsorption of sodium fluoride but not of zinc chloride, as shown by the following:[5]

Analysis of Impregnating Solution

Zinc		Fluorine	
Before, per cent	After, per cent	Before, per cent	After, per cent
1.03	1.03	1.02	0.91
0.91	0.89	0.75	0.61
0.71	0.70	0.94	0.86

Fire Retardants.—Wood cannot be prevented from burning, but its ignition temperature can be raised by impregnation with suitable salts. The protective action of the salt may be due to: (1) water of crystallization; (2) formation of a coating by fusion; and (3) formation of non-combustible gases. Salts of class 1 are of little value. Dilution of the air with non-combustible gases, other than steam, is of more importance. Glowing charcoal is extinguished when the surrounding atmosphere contains 8 per cent of carbon dioxide and 9 per cent of oxygen.[1] Glowing wood bursts into flame when the oxygen content of the atmosphere is 28 to 30 per cent by volume, and is extinguished when placed in one containing 16 volumes of oxygen.[2]

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[1] R. König, *Chem. Zentr.*, **32** (1861), 588.

[2] A. Payen, *Compt. rend.*, **58** (1864), 1033–1035.

[3] R. Nowotny, *Z. angew. Chem.*, **30** (1917), Ref. 136; *Oesterr. Chem. Ztg.*, **25** (1922), 102–104.

[4] R. Nowotny, *Oesterr. Chem. Ztg.*, **13** (1910), 81–84.

[5] Apparent adsorption is probably due to error in analysis; it is difficult to determine fluorine accurately in the presence of chlorine.

Wood will not ignite spontaneously until it is heated above the point of the exothermic reaction, which is about 275°. Sound hemlock ignited at 285° and pine at 300 to 330°. Decayed wood ignites at much lower temperatures.[3]

The ignition temperature may be taken as the point at which sufficient combustible gases are given off to cause the wood to burn; this will vary with the time and the temperature applied. Prince[4] used the temperature at which the specimens could be held for 40 minutes, before ignition by a pilot light took place.

Temperatures at Which Wood Can Be Ignited after Heating for 40 Minutes

Species	Moisture, per cent	Ignition temperature, degrees Centigrade	Species	Moisture, per cent	Ignition temperature, degrees Centigrade
Tamarack	15.0	180	Hemlock	0	180
Tamarack	0	168	Noble fir	18.0	195
Basswood	9.8	168	Noble fir	0	187
Basswood	0	168	Western larch	19.5	180
Longleaf pine	Air dry	180	Western larch	0	157
Longleaf pine	0	157	Sitka spruce	19.1	180
Red oak	11.2	157	Sitka spruce	0	157
Red oak	0	157	Redwood	19.4	180
Hemlock	18.5	157	Redwood	0	157

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[1] F. C. G. Müller, C. A., **12** (1918), 561.

[2] P. Anema, *Chem. Weekblad*, **10** (1913), 1056; W. P. Jorissen, *Ibid.*, 1057.

[3] H. B. Hill and A. M. Comey, *Proc. Am. Acad. Arts Sci.*, **22** (1886), 482.

[4] R. E. Prince, *Proc. Am. Wood-Preservers' Assoc.*, **10** (1914), 158–172; *Proc. Nat. Fire Protect. Assoc.* (1915). 106–149.

Of the various salts examined as fire retardants by Banfield and Peck,[1] ammonium phosphate was the best. Their results are given in the accompanying table.

IGNITION TEMPERATURES OF WOOD IMPREGNATED WITH SALTS

Chemical	Strength of solution, normality	Ignition temperature, degrees Centigrade	Impregnation*
Zinc chloride (2)	0.5	295	*P*
Magnesium chloride (3)	0.5	311	*I*
Calcium chloride (3)	0.5	312	*I*
Cupric chloride (1)	0.5	270	*I*
Ammonium chloride (2)	0.5	297	*I*
Bismuth chloride (1)	0.3	265	*I*
Ferric chloride (1)	0.5	284	*I*
Sodium chloride (2)	0.5	295	*I*
Ammonium sulphate (3)	2.0	317	*P*
Ammonium phosphate (3)	2.0	298	*I*
Ammonium phosphate (3)	2.0	350	*P*
Borax (3)	0.29	307	*I*
Boric acid (2)	....	299	*I*
Aluminum sulphate (2)	0.25	289	*I*
Potassium alum (1)	0.3	246	*I*
Sodium silicate (3)	0.5	322	*I*
Stannic chloride (1)	0.5	241	*I*
Zinc ammonium phosphate (3)	....	320	*V* and *P*

* *P* = pressure of 50 to 60 pounds per square inch; *I* = immersion; *V* = vacuum.

(1) Fire promoters; wood burns below 290°.

(2) No effect; wood burns between 290 and 300°

(3) Fire retarders; wood burns above 300°.

Resistance of Wood to Chemicals.—Wood is an important engineering material, due to its inertness to various chemicals in comparison with metals under the same conditions. The woods most commonly used are the following:

1. Cypress (*Taxodium distichum*).
2. Longleaf pine (*Pinus palustris*).
3. Redwood (*Sequoia sempervirens*).
4. Douglas fir (*Pseudotsuga taxifolia*).
5. Sugar maple (*Acer saccharum*).

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[1] W. O. BANFIELD and W. S. PECK, *Can. Chem. Met.*, **6** (1922), 172–176.

6. White oak (*Quercus alba*).
7. Yellow poplar (*Populus deltoides*).
8. Tamarack (*Larix laricina*).
9. White pine (*Pinus strobus*).
10. Norway pine (*Pinus resinosa*).
11. Spruce (*Picea*).

The action of various chemicals on the first six species listed has been studied by Hauser and Bahlman,[1] whose results are given in the accompanying table. The following conclusions may be drawn:

1. Acetic acid. There is only slight action at all concentrations.

2. Hydrochloric acid. A 5 per cent solution renders redwood brittle, while maple and oak are not affected until the concentration reaches 25 per cent. Cypress, fir, and pine withstand a 25 per cent acid, while all woods are destroyed by the concentrated acid.

3. Sulphuric acid. A concentration of 5.0 per cent has no effect on the woods, with the exception of redwood, which is made brittle by a 1 per cent solution. Cypress and pine are not greatly affected by a 25 per cent solution; stronger acids destroy all woods.

4. Nitric acid. A 5 per cent solution affects redwood; a 10 per cent, oak and maple, but not cypress, fir, and pine. A hot 5 per cent or a cold 25 per cent solution destroys all woods.

5. Sodium hydroxide. Maple, oak, and redwood are seriously attacked by a 1 per cent solution, though the other species withstand a 10 per cent solution. Pine alone can be used with a 25 per cent solution.

6. Sodium sulphide. A concentration of 20 per cent destroys only oak and redwood.

7. Bleaching powder. Cypress, fir, and pine are most resistant.

8. Longleaf pine is the most resistant to chemical reagents in general.

Information obtained from the chemical industries showed that for pickling tanks cypress was first choice, followed by

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[1] S. J. Hauser and C. Bahlman, *Chem. Met. Eng.*, **28** (1923), 159–163; *cf.* C. S. Robinson, *J. Ind. Eng. Chem.*, **14** (1922), 607.

PHYSICAL EFFECTS OF CHEMICALS ON WOOD
(After 1 Month in Cold and 8 Hours in Boiling Liquids)

Chemical	Concentrate, per cent	Cypress		Fir		Pine	
		Cold	Hot	Cold	Hot	Cold	Hot
$CH_3.COOH$	5	--	....	--	....	--	
	25	--	....	--	....	--	
	50	SS	....	SS	....	--	
	Glacial	SS	....	SS	....	--	
HCl	5	--	--	--	S	--	--
	10	SS	SS	SS	S	--	SS
	25	SS	VS, VB	SS	VS, VB	SS	S
	Con.[1]	VS, B, Cl	....	VS, B, GR	....	VS, B, Cl	
H_2SO_4	1	SS	S	SS	S	--	--
	5	SS	S	SS	S	--	SS
	10	SS	VS, P	S	S	SS	SS
	25	SS, SB	VS, VB	S, B	VS, VB	SS	VS, VB
HNO_3	5	--	S	SS	VS	--	S, Shd
	10	--	VS, Shd	SS	VS, Shd	SS	S, Shd
	25	S, B	VS, Shd	VS, B	VS, Shd	SS, B, Cl	S, Shd
$NaOH$	1	--	SS	--	Sh, GR	--	--
	5	--	SS	SS	Sh, GR	--	--
	10	--	SS	SS, GR	Sh, GR	SS	VH, Sh, Di, GR
	25	SS, P	SS	SS, GR, P	GR	SS	VH, GR, W
Na_2S	5	SS	....	SS	....	--	
	20	SS	....	SS	....	--	
$NaHSO_3$	10	--	....	--	....	--	
	25	--	....	--	....	--	
Na_2CO_3	5	--	SS	--	GR	--	--
	20	--	SS	--	--	GR	--
$Ca(OH)_2$	Filtered	--	....	--	....	--	
	10 susp.	--	....	--	....	--	
$Ca(ClO)_2$	Filtered	SS,FZ, GR	....	SS, FZ, GR	....	FZ	
	5 susp.	SS,FZ		SS, FZ		FZ	
$NaCl$	10	--	--	--	SS	--	--
	25	--	--	--	SS	--	--
$CaCl_2$	10	--	....	--	....	--	
	25	--	....	--	....	--	

[1] After 1 week.

SS—slightly soft
S—soft
VS—very soft
VH—very hard
SB—slightly brittle
B—brittle
– – –no noticeable action
VB—very brittle
P—pliable
SP—slightly pliable
Sh—noticeably shrunken
Ex—noticeably expanded
Cl—cracked lengthwise
W—warped
Di—considerably distorted
GR—grain raised or roughened
FZ—covered with downy "fuzz"
CH—charred
Shd—shredded, easily picked apart

PHYSICAL EFFECTS OF CHEMICALS ON WOOD.—(*Continued*)

Chemical	Concentrate, per cent	Redwood		Maple		Oak	
		Cold	Hot	Cold	Hot	Cold	Hot
$CH_3.COOH$	5	- -	......	- -	......	- -	
	25	SS	......	- -	......	- -	
	50	SS	......	- -	......	- -	
	Glacial	SS	......	- -	......	- -	
HCl	5	SS, VB	VS, B	- -	SS	- -	- -
	10	SS, VB	VS, B	- -	S	- -	SS
	25	SS, VB	VS, VB, Ch	S, B	VS, VB	SS, SB	VS, VB
	Con.[1]	VS, VB	......	VS, B, Sh, Cl	......	VS, B, Di, Ex, Cl	
H_2SO_4	1	SS, B	VS	- -	SS	- -	W
	5	VS, B	VS, B	- -	S	SS	SS
	10	VS, B	VS, VB	SS, B	S	SS, SB	SS
	25	VS, VB	VS, VB, Ch	VS, VB	VS, VB	SS, B	VS, VB
HNO_3	5	VS, VB	VS, VB	SS	VS, Shd	SS, GR	S, Cl, Shd
	10	VS, VB	VS, VB, Cl, Shd	SS, SB	VS, Shd	S, B, GR, Sh	S, Cl, Shd
	25	VS, VB	VS, VB, Cl, Shd	S, VB, Sh	VS, Shd	VS, VB, GR, Sh, Cl	S, Cl, Shd
NaOH	1	VS, W, SB, GR	S	Cl	Sh	Sh, Vh, Di	Vh, Sh, Di
	5	VS, SB, GR	S	Sh	Sh	Sh, Vh, Di, GR	Vh, Sh, Di
	10	VS, GR, P	S, Sh, Di, GR	Sh, GR, W	......	Sh, Vh, Di, GR, W, P	Vh, Sh, Di, GR
	25	SS, GR, P	S, Sh, Di, GR, B	Sh, GR, SS, P	W, GR	SS, GR, W, P	WH, GR
Na_2S	5	S, P, B	......	- -	......	SS, GR, P	
	20	S, P, B	......	- -	......	SS, GR, P	
$NaHSO_3$	10	SS	......	- -	......	- -	
	25	SS	......	- -	......	- -	
Na_2CO_3	5	- -	S	- -	- -	- -	Sh, GR
	20	- -	S	- -	- -	- -	Sh, GR
$Ca(OH)_2$	Filtered	GR	......	- -	......	GR	
	10 susp.	SS	......	GR	......	- -	
$Ca(ClO)_2$	Filtered	S, GR, B, Sh, FZ	......	SS, FZ, Sh	......	GR, FZ	
	5 susp.	S, GR, B, Sh, FZ	......	SS, FZ	......	GR, FZ, SP	
NaCl	10	SS, SB	SS, SB	- -	- -	- -	
	25	SS, SB, GR	SS, SB	- -	- -	- -	- -
$CaCl_2$	10	SS	......	- -	......	- -	- -
	25	SS	......	- -	......	- -	

[1] After 1 week.

SS—slightly soft
S—soft
VS—very soft
VH—very hard
SB—slightly brittle

B—brittle
- - -—no noticeable action
VB—very brittle
P—pliable
SP—slightly pliable

Sh—noticeably shrunken
Ex—noticeably expanded
Cl—cracked lengthwise
W—warped
Di—considerably distorted

GR—grain raised or roughened
FZ—covered with downy "fuzz"
CH—charred
Shd—shredded, easily picked apart

white pine and resinous pines, such as longleaf and Norway.[1] Close-grained, resinous longleaf pine is preferable to cypress for cold or warm dilute acids, while cypress is best for hot acids. Tanks for hydrochloric acid are given a protective coating of pitch or asphalt. Tamarack is most suitable for handling a warm, dilute (10 to 12 per cent) solution of hydrofluosilicic acid. White pine and tamarack are preferred for piping dilute organic and inorganic acids.

Hot solutions of cuprous and cupric chloride carbonize wood rapidly. Scotch pine of slow growth was more resistant than "pitch pine." Spruce had a low resistance.[2] Wood impregnated with 1.5 to 4.00 per cent solutions of zinc chloride showed a decrease in strength, especially if the temperature was raised above normal.[3]

Weathering and Natural Coloration of Wood.—On exposure to the weather wood darkens and gradually disintegrates to a powder. Certain species turn gray and acquire a silky luster. Wiesner[4] investigated these phenomena and reached the following conclusions: Moisture is essential for wood to turn gray; direct sunlight promotes the change but is not necessary; a brown color is due to transformation of the cell membrane into humus; the change of wood into a friable mass is largely limited to coniferous woods exposed in a horizontal position to atmospheric influences; the wood substance gradually changes to humus, and expansion and contraction, due to unequal distribution of moisture, produces a powder; the powder has a higher hygroscopicity and ash content than the original wood.

Attack by fungi excepted, the disintegration of wood exposed to the weather is without doubt due to the photochemical formation of brittle oxycellulose (see p. 383). The latter is reduced to a loose powder by the expansion and contraction of the wood.

The yellow coloration produced by the aging of lignified materials may be destroyed or prevented by the use of hydroxylamine or its acetate.[5]

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[1] A. W. Schorger, *Chem. Met. Eng.*, **18** (1918), 528–531.

[2] E. Jensch, *Z. angew. Chem.*, **7** (1894), 153–155.

[3] T. R. C. Wilson and E. Bateman, *Proc. Am. Wood-Preservers' Assoc.*, **17** (1921), 80–88; H. B. Luther, *Ibid.*, 89–114.

[4] J. Wiesner, *Akad. Wiss. Wien*, **49**, II (1864), 61–92.

[5] C. F. Cross, E. P. 104032 (1916).

Schramm[1] attributes the gray or green color to particles of iron, in dust transported by the wind, which react with the tannins in the wood. It has recently been shown that the gray color is due to the spores of fungi deposited in the surface cells.[2]

Freshly felled wood frequently undergoes pronounced color changes which are not always due to fungi. Linden wood turns green, the principal coloration taking place in the medullary rays and wood parenchyma.[3] The coloration is independent of temperature and takes place in summer as well as in winter. Moisture and oxygen are essential, no color being obtained in an atmosphere of ammonia or carbon dioxide. The color, presumably due to an iron tannate, is destroyed by oxalic acid and sodium hydroxide.

Von Tubeuf[4] records a special case of a living spruce tree whose sapwood, with the exception of the three to four youngest rings, was colored blue-black from the roots to the extremest branch. The phenomenon was traced to the presence of iron salts in an adjacent brook. The heartwood, through its inability to transport water, was not stained.

A striking example is the red color produced in fresh alder wood (*Alnus glutinosa*). Dreykorn and Reichardt[5] thought that "alder red" (phlobaphene) was formed by the action of an enzyme on the tannin. The coloring matter is formed only in the living cells; air and moisture are essential, but light is not.[6] Bases increase the coloration, while acids destroy it. Nothing further is known.

The sapwood of alder (*Alnus incana* Moench), white birch (*Betula populifolia*), paper birch (*Betula papyrifera*), sugar maple (*Acer saccharum*), and red gum (*Liquidambar styraciflua*) stain various shades during spring and summer. Alder and birch stain a reddish yellow or rusty color in a few minutes during hot, humid weather. Bailey[7] thought that the color was due to the action of oxidizing enzymes, since no color was obtained if the woods were boiled in water.

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[1] W. H. Schramm, *Jahresber. Ver. angew. Bot.*, **4** (1906), 140–163.

[2] M. Mobius, *Ber. botan. Ges.*, **42** (1924), 15–18.

[3] F. W. Neger, *Naturwiss. Z. Forst. u. Landw.*, **8** (1910), 305–313.

[4] C. von Tubeuf, *Naturwiss. Z. Forst. u. Landw.*, **9** (1911), 273–276.

[5] F. Dreykorn and E. Reichardt, *Dinglers polytech. J.*, **195** (1870), 157–171.

[6] F. W. Neger, *Naturwiss. Z. Forst. u. Landw.*, **9** (1911), 96–105.

[7] I. W. Bailey, *Botan. Gaz.*, **50** (1910), 142–147.

Judd[1] investigated the brown stain obtained during the kiln drying of green, frozen sugar maple and concluded that enzymes played no part. The wood did not discolor in the presence of hydrogen peroxide, carbon dioxide, sulphur dioxide or steam in the absence of oxygen. Wood treated with hot water, steam, and various germicides always stained under the influence of a warm, humid atmosphere. The color began at the surface and traveled throughout the wood. Staining could be prevented by the use of a low temperature (50 to 55°) and low humidity (60 per cent).

Western yellow pine and sugar pine stain during kiln drying, unless a low temperature is used. The stain is not on the surface, but 1 to 2 millimeters beneath it. In this case, the substances producing the stain appear to be carried towards the surface of the board by water, and deposited where it escapes as steam.

Artificial Coloration of Wood.—At elevated temperatures, wood acquires a permanent brown color, due to incipient destructive distillation.[2] Prolonged heating in sealed tubes at 90 to 100° produces a similar darkening. This may be due to tannin, since tannic acid began to decompose after 24 hours' heating, and after 264 hours, was converted into a black mass.[3] Oak wood, heated intermittently in a water oven for several weeks, gradually darkened and acquired the brown color of old oak.[4]

Woods rich in tannin rapidly turn brown on exposure to fumes of ammonia.[5] The color is permanent and extends to a depth of 2 to 3 millimeters. Woods poor in tannin may be treated with a hot 5 to 10 per cent solution of pyrogallol before "fuming" with ammonia.[6]

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[1] R. C. Judd, *J. Ind. Eng. Chem.*, **7** (1915), 920.

[2] H. F. Weiss, U. S. P. 1366225 (1921); Reissue 15316 (1922).

[3] E. Knecht, *J. Soc. Dyers Colourists*, **36** (1920), 195.

[4] C. K. Tinkler, *Biochem. J.*, **15** (1921), 484.

[5] W. Kolitsch, *Mitt. k.k. techn. Gewerbe-Mus. Wien*, **11** (1901), 79–80.

[6] H. Wislicenus. *Z. angew. Chem.*, **23** (1910), 1441–1446.

In the absence of oxygen, oak acquired a reddish color, which changed to the brown of fumed oak on exposure to air.[1] Methylamine and trimethylamine behaved like ammonia. The amount of ammonia taken up by oak during fuming was:

	N		NH_3	
	Natural oak, per cent	"Fumed" oak, per cent	Calculated addition, per cent	Found by distillation with NaOH, per cent
Japanese oak..........	0.353	1.75	1.69	1.64
English oak...........	0.308	2.72	2.90	2.23

When 10 grams of oak shavings were covered with dilute ammonia and exposed to 100 cubic centimeters of air, the following volumes of oxygen were absorbed in a given time:

Time, minutes................	5	15	60
English oak, cubic centimeters..	2.6	5	10
Japanese oak, cubic centimeters.	3	7	10

The absorption of oxygen was complete (21 cubic centimeters) on standing overnight.

The color effects of age may be obtained by imbedding the wood in alkaline soil;[2] heating it while imbedded in a mixture of lime or calcium carbonate and ammonium salts;[3] and with dry ammonia.[4] Kleinstück[5] proposes to season and color wood by subjecting it to aldehydes and ketones in the gaseous state, in the presence of ammonia, whereby condensation products are formed with the protein and tannins. Oxides of nitrogen produce a golden shade.[6]

Dyeing Wood.—Wood seldom dyes uniformly, owing to its structure and lack of chemical homogeneity. In most cases the resistance to the penetrance of dyes is great, even under pressure. Dyestuffs dissolved in water and organic solvents seldom penetrate wood more than 0.5 to 2 millimeters.[1] Oak does not dye satisfactorily by immersion, but pine is penetrated to a depth of 5 to 20 millimeters in 8 days. Maple, linden, and poplar give uniform colors. Pear wood is used for imitation ebony. Beech is one of the most satisfactory woods for dyeing, as only slight pressures are required. The greatest penetration is obtained by the use of crystalline, water-soluble dyes, but these are seldom fast to light.

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[1] C. K. Tinkler, *Biochem. J.*, **15** (1921), 477–486.

[2] K. K. Schmidt, E. P., 18558 (1907).

[3] K. K. Schmidt *et al.*, U. S. P. 1012283 (1911); 1057284 (1913); Deutsche Werkstätten für Handwerkskunst, F. P. 425085 (1911).

[4] H. W. de Prez, U. S. P. 1015008 (1912).

[5] M. Kleinstück, U. S. P. 1210491 (1917).

[6] L. Doyen, E. P. 1063 (1913).

The wood of the standing tree may be colored by introducing dyestuffs or chemicals at the base and allowing them to be transported by the sap.[2] Aniline dyes, the suitability of which must be determined by experiment, may be employed. Malachite green and methylene blue stain uniformly, while eosin forms streaks. The salts of certain bases color wood by reacting with the lignin. Aniline hydrochloride colors wood yellow, while *p*-phenylenediamine gives a salmon red. Birch trees are colored overnight, even as far as the leaves, by a 1 per cent solution of aniline hydrochloride. Tannic acid is one of the few chemicals that may be used to produce a definite color tone on subsequent treatment with other substances.

Action of Light.—The deteriorating action of light on mechanical pulp is mentioned below. The increase in acidity is pronounced, showing that oxidation has taken place. The products resulting from the action of light on cellulose are grouped under the indefinite heading of oxycellulose, for want of a better term.

Harrison[3] has studied the effects on cellulose of the action of sunlight, mercury light, and radium emanations. Radium emanations are especially destructive. The products formed are of the nature of hydroxy-acids, and have a strong reducing action. In this way is explained the reduction or fading of dyestuffs in cloth.

The fading action of the sunlight on dyed wood does not penetrate to a depth exceeding 0.03 to 0.06 millimeter.[4]

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[1] F. Moll, *Z. angew. Chem.*, **29** (1916), 405–409; M. de Keghel, *Rev. gen. chim.*, **14** (1911), 348–355.

[2] M. Kleinstück, *Z. angew. Chem.*, **26** (1913), Aufsatz., 239–240; L. S. Gardner, U. S. P. 952245 (1910).

[3] W. Harrison, *J. Soc. Dyers Colourists*, **28** (1912), 225–236; **30** (1914), 206–211.

[4] W. H. Schramm and A. Jungl, *Farber-Zeit.*, **17** (1906), 333–342.

Cotton fabric exposed at a temperature of 30 to 35° to the light from a Cooper-Hewitt mercury vapor lamp, which gives a large amount of ultra-violet light, turned yellow and showed all the properties of oxycellulose.[1] Disintegration is attributed to a specific physical action, while the oxidation may be due to the formation of ozone.

It may be mentioned that wood has a pronounced action on photographic plates in the dark, and produces its own image after exposure for 0.5 to 18.0 hours at temperatures up to 55°. Charring of the wood on one side causes it to become highly active.[2] The active substance appears to occur in the layer between the charcoal and the wood.[3] Activity was exercised through paper, but not through sheets of glass and metal.

Russell,[4] found that all woods were active, especially the conifers; this may be explained by the presence of resins which have the same action.[5] Tannins, essential oils, and other organic compounds are effective.[6] Oak, beech, Spanish chestnut, and sycamore were very active, but ash, elm, and horse chestnut only slightly so. The spring wood of Scotch pine affects the plate, but the autumn wood does not, unless it is powdered; in the larch, the condition is reversed. Oak wood 100 years old was still active, as well as the central portion of a piece of oak taken from a Dartmoor bog. The activity of all woods could be greatly increased by exposing them to sunlight. Blue light was as effective as white, but red and green were not stimulating.

The exact nature of the phenomenon has not been ascertained. It is not due to radioactivity, since a sheet of glass or mica 0.001 inch thick entirely prevents action. Russell is of the opinion that the active agent is hydrogen peroxide, since it will pass through porous bodies and gelatin.

Action of Oxidizing Agents.—Reagents such as hydrogen peroxide,[7] nitric acid, potassium chlorate, a mixture of nitric acid and potassium chlorate, etc. have been used for bleaching wood. The light color obtained is seldom permanent.

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[1] C. Dorée and J. W. W. Dyer, *J. Soc. Dyers Colourists*, **33** (1917), 17–19.

[2] W. J. Russell, *Proc. Roy. Soc.*, **61** (1897), 424–433.

[3] D. Isitani, *Physik. Z.*, **10** (1909), 1003–1005.

[4] W. J. Russell, *Proc. Roy. Soc.*, **74** (1904), 131–134; *Trans. Roy. Soc.*, **197**B (1905), 281–289.

[5] E. von Aubel, *Compt. rend.*, **138** (1904), 961–963.

[6] H. M. Ward, *Proc. Cambridge Phil. Soc.*, **13** (1904), 3–11.

[7] C. Marggraf, *Kunststoffe*, **7** (1917), 165.

When potassium persulphate was run into a dilute potassium hydroxide solution in which pine wood was being digested at a temperature of 60 to 65°, the odor evolved was almost unendurable.[1] A potassium hydroxide solution containing wood gave an odor of vanillin or coumarin on electrolysis.

The action of ozonized oxygen, containing about 1 per cent of ozone, on beech wood shavings has been investigated by Dorée and Cunningham.[2] Unlike jute, the wood was not bleached. Ozone attacked the wood rapidly, rendering it friable and producing a nauseous odor through the formation of organic acids which were partly volatile in steam. Ozone had practically no action on dry wood, but in the presence of moisture there was at first a rapid formation of organic acids followed by a drop to one-tenth of the initial value. Carbon dioxide was produced continuously, there being little decrease in rate after 6 hours. The volatile acids, consisting of acetic, formic, and another acid having reducing properties, amounted to 2.6 per cent, calculated as acetic acid. The non-volatile acid liquor had an acidity three to five times greater than the value for volatile acids. Oxalic acid and phenols were absent. The solution contained reducing substances of an aldehydic or ketonic character. Ozonization for 36 hours produced a loss in weight of 40.8 per cent. The residue had a high copper number; it gave a large amount of furfural, but contained only a small amount of methoxyl. The absence of vanillin indicates that lignin does not contain a coniferyl alcohol group as postulated by Klason. It is claimed that wood may be seasoned by treatment with ozonized air,[3] but it is not apparent wherein benefit would accrue.

Smith[4] has studied the deterioration of mechanical pulp under the influence of sunlight, ozone, and temperature. The paper was placed between glass plates, thus excluding most of the ultra-violet rays, and exposed to the sun for 75 hours. The similarity of the results indicates that the deterioration was due in all cases to oxidation.

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[1] L. Meyer, *Chem. Ztg.*, **31** (1907), 902.

[2] C. Dorée and M. Cunningham, *J. Chem. Soc.*, **103** (1913), 677–686.

[3] M. P. Otto, E. P. 133263 (1919); G. F. Lyon, E. P. 182504 (1921).

[4] W. H. Smith, "Studies on Paper Pulps," *Bur. Standards, Tech. Paper*, **88** (1917), p. 11.

EFFECT OF DETERIORATION ON MECHANICAL PULP

	Original pulp	Sunlight	Ozonized air	100° for 20 hours	150° for 20 hours
Methoxyl (per cent).	5.10	4.60	4.74	4.75	4.48
Furfural (per cent). .	6.23	5.41	5.82	5.72	4.64
Copper number (corrected)	2.0	7.6	10.9	3.00	11.9
Acid number........	16.1	51.0	63.2	27.0	63.0

An interesting case of the formation of oxalic acid has been called to the writer's attention. A locust insulator pin supporting a high-tension wire (22,000 volts) on the Boston and Maine Railroad was converted to oxalic acid to a considerable extent. Since ozone does not appear to produce oxalic acid in quantity, the active agent must have been nitric acid produced from atmospheric nitrogen.

Wood is capable of yielding small quantities of iodoform. Schorger[1] obtained iodoform from the solution resulting from grinding aspen in dilute alkali, and suggested that the parent substance might be acetone. Huebner and Sinha[2] treated 200 grams of poplar wood with 4 per cent of its weight of iodine in the form of iodine-potassium iodide solution, let stand several hours, added dilute sodium hydroxide and steam distilled; 0.25 gram of iodoform was obtained. Since cotton and purified wood cellulose continued to give iodoform on re-treatment, it is evident that some of the iodoform originates from the cellulose molecule.

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[1] A. W. SCHORGER, *J. Ind. Eng. Chem.*, **15** (1923), 812.

[2] J. HUEBNER and J. N. SINHA, *J. Soc. Chem. Ind.*, **42** (1923), 258T.

CHAPTER XII

PULP PROCESSES AND WOOD PULPS

Wood, for purposes of illustration, may be likened to honeycomb, on the wall (lignin) of which thin layers of a mixture of cellulose and lignin have been deposited to form the fibers. The framework in wood, known in a broad sense as the middle lamella, consists essentially of lignin admixed with hemicelluloses. Processes for producing pulp are based on the use of chemicals which will dissolve the strongly adhering middle lamella and leave the cellulose fibers in the form of loose bundles. Microscopic examination of thin sections of wood which have been subjected to the action of various chemicals should give valuable information on structure and the course of disintegration. A beginning in this direction has been made.[1]

Sulphite Process.—The cooking liquor in the sulphite process contains sulphurous acid as the active constituent, though bisulphites are present also. The sulphite liquor is prepared by burning pyrites or sulphur. The gas containing the sulphur dioxide is washed with water at a temperature of 50° to 75° to remove dust and sulphur trioxide, and passed up a tower containing limestone or dolomite over which water trickles. In this way a solution of calcium and magnesium bisulphites is obtained. In comparison with the calcium salt, magnesium bisulphite is more soluble and stable, and in case of the formation of sulphuric acid, gives the readily soluble magnesium sulphate. Pulps prepared with magnesium bisulphite resemble those obtained with sodium sulphite. The tower liquor is fortified with sulphur dioxide to the point desired before being used in the digester.

There are three modifications of the sulphite process, the Mitscherlich, Ritter-Kellner, and "quick cook." The liquor for the Mitscherlich process contains 2.8 to 3.8 per cent total sulphur dioxide, of which 1.7 to 2.7 per cent is free and 1.1 per cent combined. Indirect heating by steam coils is employed, the steam pressure being 85 to 110 pounds. The temperature within the digester reaches 105° in 5 hours, 130° in 12 hours, and 135° in 16 to 24 hours, at which time the cook is completed. The pressure within the digester is 45 to 60 pounds. In the Ritter-Kellner process, the liquor contains 4 per cent total sulphur dioxide, of which 2.7 per cent is free. Live steam is introduced into the digester, where a temperature of 100° is reached after 3 hours. The maximum temperature of 140 to 150° is reached in 8 hours and the cook completed in 15 hours. The pressure within the digester is 60 to 80 pounds. The "quick cook" is completed in about 8 hours. The liquor contains 5.0 to 5.5 per cent total sulphur dioxide, of which 1.2 per cent is combined. The internal pressure is about 90 pounds and a maximum temperature of 155° is reached.

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[1] A. Abrams, *J. Ind. Eng. Chem.*, **13** (1921), 786; G. J. Ritter, *Ibid.*, **17** (1925), 1194–1197.

Ordinarily, 30 to 40 per cent of the sulphur dioxide charged into the digester is recovered during release of pressure. In European practice, the sulphur actually consumed is 110 to 120 pounds per ton of wood, while in America, where the "quick cook" is mainly used, consumption runs from 120 to 180 pounds. The yield of pulp varies from 40 to 50 per cent.

Uniform penetration of the chips before heating contributes greatly to the success of the cook. The swelling of wood varies directly as the quantity of sulphurous acid in the liquor.[1] Wood will in most cases absorb about 250 parts of liquor, though extreme variations of 150 to 500 parts may be obtained. The wood should be neither too dry nor too wet; if too dry, it will absorb very little liquor. Impregnation is facilitated by the use of "wetting" compounds, such as Turkey red oil and other sulphonated oils which reduce the surface tension of aqueous solutions. If wood is impregnated with bisulphite solution, preferably by hydraulic pressure, at temperatures between 50 and 100°, 70 to 80 per cent of the bisulphite is adsorbed and retained by the wood during subsequent heating.[2] After thorough impregnation, the temperature may be raised rapidly to 140° and the digestion completed in 1.5 to 2.0 hours.

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[1] C. G. Schwalbe, *Wochbl. Papier-Fabr.*, **54** (1923), 22–23.

[2] C. G. Schwalbe, *Papierfabr.*, **21** (1923), 493–495.

Klason,[1] in 1893, advanced the hypothesis that the action of sulphite liquor consisted in the union of sulphurous acid with double bonds and aldehyde groups in the lignin, with the formation of sulphonic acids. It had been shown by Lindsey and Tollens[2] that in spent sulphite liquor the sulphur was present as the sulphonic acid. The formation of suphurous acid by dilution, and also after titration of the free acid present with iodine, indicates, in addition, a typical aldehyde addition compound.[3]

Complete extraction of the lignin from 100 grams of spruce wood should theoretically require 7.91 grams of sulphurous acid and 3.46 grams of calcium oxide.[4] In commercial operations, due to incomplete saturation of the aldehyde group in α-lignin, only 7.6 grams of sulphur dioxide and 3.2 grams of calcium oxide are consumed. Only α-lignin (acrolein-lignin) is capable of combining loosely with sulphur dioxide. Of the total 30 per cent of lignin in spruce, two-thirds consists of α-lignin and one-third of β-lignin. It has been found that in cooking 100 grams of wood the loosely combined sulphur dioxide is 3.5 grams.[5] On the basis of one molecule of sulphur dioxide to one molecule of α-lignin ($C_{22}H_{22}O_7$ = mol. wt. 398), there is present in the wood 21.7 per cent of α-lignin. This is in fair agreement with Klason's figure of 19.0 per cent.

Cross and Engelstad[6] consider the mechanism of the sulphite process as mainly one of direct sulphonation. Wood can be satisfactorily pulped with sulphurous acid alone, using a concentration of 7 per cent and a temperature of 100 to 115°, over a period of 15 to 48 hours. Sulphuric acid should be absent. "The secondary effect differentiating the by-products of the sulphurous acid and bisulphite processes are those of the degree of sulphonation, deoxidation of the CO group, and condensation of the sulphonated complex." The waste liquors from the sulphurous acid method differ from those obtained by the calcium bisulphite method in their capacity to form gels and in their tanning properties.[1]

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[1] P. Klason, *Teknisk Tids.*, (1893), 17; *cf. Svensk Kem. Tid.*, **9** (1897), 133; *Chem. Ztg.*, **21** (1897), 261.

[2] J. B. Lindsey and B. Tollens, *Ann.*, **267** (1892), 341.

[3] W. Kerp and P. Wöhler, *Arb. kais. Gesundh.*, **32** (1909), 120–143.

[4] P. Klason, *Ber.*, **53** (1920), 1869.

[5] E. Hägglund and C. B. Björkmann., *Svensk Kem. Tid.*, **36** (1924), 137.

[6] C. F. Cross and A. Engelstad, *J. Soc. Chem. Ind.*, **43** (1924), 253–257T; E. P. 12943 (1922).

The secondary reactions taking place in the sulphite process are exceedingly complex and their nature entirely unknown. It is possible to obtain twice the actual consumption of sulphur dioxide in one case as in another; yet the pulps obtained are similar in yield and properties. According to Fuchs,[2] there is no satisfactory theory of the sulphite process, and in the main this is correct. Klason's hypotheses, however, form the best working basis available.

While the main reaction may be sulphonation, Miller and Swanson[3] consider hydrolysis important. Cooks were made at a temperature of 145°, with a total sulphurous acid concentration of 3.80 per cent, of which 2.40 per cent was free and 1.40 per cent combined. Removal of the lignin practically ceased at the end of the eleventh hour; yet the pulps were not of good quality. This was not due to cessation of sulphonation, since the organically combined sulphur continued to increase with time. With a liquor containing 5.60 per cent total sulphur dioxide, of which 4.46 per cent was free, the conditions were favorable for hydrolysis and good pulps were obtained. In fact, the opinion is expressed that the chief reaction in the sulphite process is hydrolytic.[4] The factor having the greatest influence on the yield and character of the pulp is the free sulphur dioxide present. While a certain amount of combined sulphur dioxide is essential to a successful cook, the combination of the base and sulphur dioxide with the lignin are phenomena of secondary importance.

Much botanical and chemical evidence indicates that there is no chemical union between the lignin and the cellulose. In a sulphite cook, simultaneously with sulphonation of the lignin, hydrolysis of hemicelluloses and a portion of the cellulose takes place, but this may be of minor importance. Some of the hemicelluloses appear to be intimately associated with the lignin. Whether the successful removal of the lignin depends on the hydrolysis of this portion of the hemicelluloses, is unknown.

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[1] C. F. Cross and A. Engelstad, E. P. 202016 (1922).

[2] W. Fuchs, *Ber.*, **54** (1921), 484–490.

[3] R. N. Miller and W. H. Swanson, *Paper Trade J.*, **74**, 15 (1922), 295–305.

[4] R. N. Miller and W. H. Swanson, *Paper Trade J.*, **77**, 14 (1923), 51–52.

Temperature has greater influence on the progress of the pulping reaction than the concentration of the acid.[1] Changes in temperature that are commercially feasible are of greater effect than any changes in the acid concentrations within the usual range of technical practice. In the ordinary cook the relation between pressure, temperature, and acid concentration are such that the beneficial effect of increase in acid concentration are largely offset by pressure and temperature limitations, so that temperature is left as the dominant factor in controlling the progress of the reaction. The lowest average temperature that will give the requisite purification, in the necessary length of cook, will produce the best quality of pulp.

In obtaining[2] the experimental data given below, the cooking liquor contained 5.50 per cent of sulphur dioxide, of which 4.30 per cent was free and 1.20 per cent combined. The temperature was brought to 110° in 1.5 hours and uniformly raised to 148° in 8.5 hours. It will be noted that the results are very uniform in spite of the variation in pressure, hence concentration of acid.

Yield and Composition of Pulps

Cook	Pressure per square inch, pounds	Yield of screened pulp, per cent	Lignin in pulp, per cent	Cellulose in pulp, per cent	Yield of cellulose based on wood, per cent
3050	65	48.3	1.7	94.6	45.7
3051	70	48.4	2.5	96.4	46.7
3056	75	48.2	1.1	96.1	46.5
3057	80	48.2	1.2	95.9	46.2
3071	100	47.7	1.5	95.3	45.5

Contrary to the general opinion, the maximum removal of lignin in a quick cook does not occur towards the end of the cook.[3] Removal of lignin takes place at considerable speed at temperatures slightly above 100° and proceeds rapidly from this point to the end of the cook, which under the conditions obtaining in the particular experiments was at the end of the eleventh hour. The loosely combined sulphur dioxide reached a maximum at this point and then decreased. It was found that the point of maximum production of loosely combined sulphur dioxide was an excellent indication of the end of the cook. This point does not show that a good pulp will be obtained, but does indicate clearly the uselessness of continued cooking.

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[1] R. N. Miller and W. H. Swanson, *Paper Trade J.*, **78,** 15 (1924), 178–181.

[2] R. N. Miller and W. H. Swanson, *Paper Trade J.*, **79,** 16 (1924), 48.

[3] R. N. Miller and W. H. Swanson, *Paper Trade J.*, **74,** 15 (1922), 298.

Decrease in combined sulphur dioxide may take place at too high temperatures or pressures. Seidel[1] assumes that wood reacts with sulphurous acid as follows:

$$X.CH{:}CH.Y + H_2SO_3 \rightarrow X.CH_2.CH.SO_3H.Y.$$

At higher pressures decomposition takes place in accordance with the equation:

$$X.CH_2.CH.SO_3H.Y \rightarrow X.CH_2.CHOH.Y + SO_2.$$

There is thus formed a compound with a greater hydroxyl content than that of the original lignin.

In cooking by the Mitscherlich process, using indirect heating, all conditions being identical except time, a rapid drop in lignin does not occur until after the ninth hour.[2] At the end of the

MITSCHERLICH SULPHITE COOKS

(Maximum temperature, 145°; total SO_2, 3.8 per cent; combined SO_2, 1.4 per cent)

Cook No.	Duration, hours	Yield of pulp, per cent	Solubility in 1 per cent NaOH, per cent	Lignin, per cent	Cellulose, per cent	Lignin lost, per cent	Cellulose lost, per cent
Wood	.....	....	15.1	28.3	58.4		
630	7	80.8	14.8	20.9	50.2	7.4	8.2
629	9	62.8	11.2	12.0	45.9	16.3	12.5
626	10	64.0	8.4	10.6	49.2	17.7	9.2
625	11	51.0	7.3	3.9	43.7	24.4	14.7
634	11.5	50.6	5.7	4.6	44.2	23.7	14.2
633	12	51.2	5.6	3.8	45.1	24.5	13.3
631	12.5	51.6	5.9	2.5	46.7	25.8	11.7
632	13.25	47.1	5.3	3.0	42.7	25.3	16.7
636	15	48.4	5.3	0.9	43.1	27.4	15.3

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[1] H. SEIDEL, *J. Soc. Chem. Ind.*, **19** (1900), 1033.

[2] M. W. BRAY and T. M. ANDREWS, *Paper Trade J.*, **76**, 3 (1923), 49–52.

seventh hour losses of lignin and of cellulose are about equal, but from this point on, the lignin disappears faster than the cellulose. The portion of the wood soluble in 1 per cent sodium hydroxide shows little decrease up to the ninth hour. Removal of lignin is always accompanied by loss of cellulose, and it does not appear possible to obtain more than 45 per cent of cellulose by present commercial methods of cooking. According to Sieber,[1] the loss based on total cellulose is of the order of 11 to 12 per cent.

The amount of combined sulphurous acid present in the cooking liquor is of great importance. Cooks made with a total sulphur dioxide content of 5.0 per cent, of which 0.30 to 2.09 per cent was combined with lime, showed that the combined sulphur dioxide must not be less than 1 per cent; if lower, the screenings, color, and bleach consumption of the pulp are increased.[2] Beyond 1 per cent combined sulphur dioxide, these factors remain constant. In the case of incompleted cooks, the spent liquor may contain only half of the base originally present.[3] The remainder is largely present in the pulp, apparently organically combined, in a form slightly soluble or slowly diffusible. In the first stage of the cook the ash content rises from 0.48 to 1.8 per cent.[4] This localization appears to be independent of the acid content of the liquor, but is largely influenced by the moisture content of the wood, and varies inversely to it. All other conditions being equal, the wetter wood gives a higher yield and a better pulp, though a longer cooking period is required.

The consumption of sulphur dioxide may vary greatly. With a low content of calcium oxide, *e.g.*, 3 grams per 100 grams of wood, the wood can be completely pulped with the consumption of 9 grams of suphur dioxide.[5] This is the lowest amount that should be used in practice. The sulphur dioxide consumption increases with the amount of calcium oxide present up to 4.8 grams, after which there is no essential difference between the limits 4.8 to 7.2 grams of calcium oxide. In general, the higher the sulphur dioxide content of the liquor, the greater is the consumption of sulphur dioxide. The loosely combined sulphur dioxide is 3.5 grams per 100 grams of wood. The yield of pulp calculated on the calcium oxide content of the cooking liquor is greatly dependent on the uniformity of the wood. If the lime content is too high, a large excess of sulphur dioxide is required to bring the cook to completion in the usual time.

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[1] R. Sieber, *Papier-Fabr.*, **22** (1924), 243.

[2] S. E. Lunak, "Effect of Varying Certain Cooking Conditions in the Production of Sulphite Pulp from Spruce," *U. S. Dept. Agr. Bull.*, **620** (1918).

[3] R. N. Miller and W. H. Swanson, *Paper Trade J.*, **76,** 9 (1923), 49–51.

[4] C. G. Schwalbe, *Zellstoff u. Papier*, **1** (1921), 11.

[5] E. Hägglund and C. B. Björkmann, *Svensk Kem. Tid.*, **36** (1924), 133–135.

The chemical and mechanical properties of the pulp depend on the composition of the liquor and the manner of heating, but especially on whether available sulphite (calcium bisulphite) is present at the end of the cook.[1] Immediately or sometime after disappearance of the available sulphite, not only the pulp but the composition of the liquor changes greatly. With a relatively high initial lime content and moderate amount of sulphur dioxide, a pulp of the greatest strength is obtained if the cook is stopped shortly after disappearance of the available sulphite. With increasing concentration of sulphur dioxide, the proper time for stopping the cook is thrown nearer the point of vanishment of the available sulphite.

Within wide limits of composition of the cooking liquor, with respect to calcium oxide and sulphur dioxide, the same yield of pulp, namely, 48 to 49 per cent, is obtained if the cook is stopped at the proper time. The copper number of the pulp increases with the amount of lime present. After disappearance of the available sulphite, the Tingle bromine number of the pulps increases slowly and then suddenly drops at a certain moment. At this point, the pulps show greatly decreased strength. The amount of sulphur dioxide firmly bound, and hence to be considered as a measure of the sulphur consumption, increases greatly as the concentration of sulphur dioxide increases. An acceleration of this combination of sulphur dioxide sets in after disappearance of the available sulphite.

According to Miller and Swanson,[2] the reactions involving the combination of the base and the sulphur dioxide with the organic matter are more or less independent of the reactions governing the yield and quality of pulp, and no rule can be laid down for them. Comparable pulps can be obtained with a sulphur consumption varying from 262 to 455 pounds of sulphur per ton of dry pulp. The number of pounds of lignin removed per pound of sulphur in organic combination varied from 5.44 to 6.55. The data on loosely combined sulphur contributed little to a knowledge of the reactions going on within the digester. The values for loosely combined sulphur, while approaching a constant, have no apparent bearing on the quality of the pulp, and probably represent reactions independent of the main pulping reactions.

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[1] E. Hägglund, *Svensk Kem. Tid.*, **36** (1924), 284–294.

[2] R. N. Miller and W. H. Swanson, *Paper Trade J.*, **76**, 10 (1923), 51–54.

It has been found that wood which has been boiled with very dilute mineral acid resists resolution by the sulphite process. The stronger the acid, the more resistant becomes the wood. The same effect is produced if pine wood is given a preliminary boiling with 2 to 8 per cent of sodium hydroxide.[1] Coniferous wood, in particular, gives a poor cook with sodium sulphite if free sodium hydroxide is present within certain limits.[2] Apparently, the lignin is resinified by the action of acids and alkalis on the aldehyde (?) group and double bonds, so that it has lessened capacity to react with sulphite liquor.

This peculiarity of lignin, apparently, has a direct connection with irregularities in the cooking process, such as the formation of dark liquors and pulps. Klason[3] in his early work calculated that 1 kilogram of wood is capable of combining with 105.6 grams of sulphur dioxide and 45 grams of calcium oxide. In practice, only about 75 per cent of these amounts are used, since half of the theoretical amount of sulphur dioxide would form unstable sulphonic acid groups. In order, therefore, to obtain a successful cook, it is necessary to have at least 22.5 grams of calcium oxide present to combine with the stable ligninsulphonic acids, which are strong acids.

A cook was made, using 131 grams of total sulphur dioxide and 45.2 grams of calcium oxide per kilogram of wood. The liquor contained a total of 3.40 per cent of sulphur dioxide, of which 2.10 per cent was free and 1.08 per cent combined. The spent liquor contained:

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[1] R. Michel-Jaffard, *Chimie & Industrie,* **11** (1924), 557–566.

[2] Information from Forest Products Laboratory.

[3] P. Klason, *Wochbl. Papierfabr.,* **41** (1910), 464–468, 541–546.

CaO in solution, grams	CaO as $CaSO_4$, grams	SO_2 as SO_3, grams	SO_2 as S, grams	SO_2 free, grams	SO_2 in lignin, grams
18.8	23.7	27.1	13.5	6.75	90.4

The presence of free stable ligninsulphonic acid or sulphuric acid causes resinification of the lignin. Sulphuric acid is formed by heating sulphurous acid, the reaction taking place rapidly above 150°: $3SO_2 = 2SO_3 + S$. Removal of the sulphuric acid by the lime promotes the above reaction, so that neither too much lime nor too much free SO_2 should be present. For the best cooking conditions, the free sulphur dioxide should be 70 per cent of the total. Free sulphur is a catalyst for the formation of sulphuric acid from sulphur dioxide, though selenium is 500 times more powerful.[1] The activity of selenium is due to the simultaneous presence of iron oxide carried over during the burning of seleniferous pyrites.[2]

The reactions involving the removal of lignin are intimately associated with the hydrogen-ion concentration of the sulphite liquor.[3] The p_H of the average sulphite liquor is about 1.5.[4] On heating, this value drops rapidly to 1.3. In order to obtain a pulp of maximum strength, p_H 1.2 should not be exceeded.

Oman[5] states that the greater the hydrogen-ion concentration, the darker is the color of the sulphite liquor. Under conditions obtaining in the usual sulphite cook, the color depends on the concentration of sulphurous acid in excess of that required to form calcium bisulphite, and is otherwise independent of the amount of lime present. According to Hägglund,[6] the formation of dark liquors does not necessarily mean a dark pulp, nor can it be assumed that the two phenomena have the same origin. The dark color of the liquor shows that all the calcium bisulphite has been consumed, while the dark color of the pulp indicates, in addition, that the hydrogen-ion concentration has reached a certain value. Free ligninsulphonic acid and sulphuric acid are then present in considerable amounts. The formation of sulphuric acid is not understood, though copper, iron, and lead are potent catalysts.

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[1] P. Klason, *l.c.*; P. Klason and H. Mellquist, *Papier-Fabr.*, **11** (1913), 145–148.

[2] J. C. Torgersen and C. Bay, *Papier-Fabr.*, **12** (1914), 483–484.

[3] P. Klason, *Svensk Kem. Tid.*, **33** (1921), 141.

[4] R. N. Miller and W. H. Swanson, Unpublished data.

[5] E. Oman, *Chem. Ztg.*, **39** (1915), 820.

[6] E. Hägglund and C. B. Björkmann, *Svensk Kem. Tid.*, **36** (1924), 140.

In a normal cook, the formation of sulphuric acid is relatively insignificant. Harpf[1] found only a slight amount of calcium sulphate in the finished cook. Miller and Swanson,[2] using a raw sulphite liquor containing 0.11 per cent sulphuric acid, obtained 0.28 per cent of sulphuric acid in the spent liquor from a cook lasting 15.75 hours. The formation of sulphuric acid appears to be independent of temperature, but related to the concentration of free sulphur dioxide.

In view of the action of strong acids on lignin, a proposed variation in the sulphite process is of interest. This consists in boiling the wood with 1 per cent sulphuric acid at 115° for 2 to 4 hours before heating with sulphite liquor.[3] Waentig[4] found that if fine shavings were subjected to the acid treatment, then chlorinated to remove the lignin, there was obtained 41 to 42 per cent of cellulose resembling hydrocellulose in its brittleness. Chips, on the other hand, gave 48 per cent of long, strong fibers. The difference is attributed to transverse cutting of the fibers in the shavings, whereby the interior of the cells was attacked. Whether boiled with acid or not, the cellulose from both shavings and chips contained uniformly 84 to 85 per cent of α-cellulose. Sulphite pulp after heating with acid showed only 74.3 per cent of α-cellulose. The cellulose from the acid-treated wood, when converted into viscose, showed a decidedly lower viscosity. The heterogeneous character of massive wood appears to protect it from brittleness on treatment with acid, although the resulting cellulose manifests a higher chemical activity.

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[1] A. Harpf, "Beiträge zur Kenntnis der chem. Vorgänge beim Sulfitverfahren," Diss. Bern (1892), p. 26.

[2] R. N. Miller and W. H. Swanson, *Paper Trade J.*, **76**, 10 (1923), 53.

[3] E. Bronnert, U. S. P. 1392047 (1921).

[4] P. Waentig, *Zellstoff u. Papier*, **2** (1922), 152–155.

By-products.—The volatile oil obtained in cooking coniferous wood by the sulphite process contains some *l*-borneol,[1] but consists largely of cymene, as was first shown by Klason.[2] The yield varies from 0.36 to 1.0 gallon of oil per ton of pulp.[3] According to Kertész,[4] the oil contains 80 per cent of cymene, the remainder being a mixture of sesquiterpene and diterpene. These hydrocarbons were believed to be formed from terpenes and resins by the reducing action of the sulphite liquor, accompanied by polymerization, isomerization, and dehydration. Cross and Engelstad[5] shared the general belief that cymene was formed by the direct action of sulphurous acid. A tube containing aqueous sulphur dioxide and turpentine, heated at 110° for 26 hours, showed the presence of sulphur. It was assumed that there was a slight conversion to cymene. The formation of cymene appears, however, to be due to oxidation by sulphur set free during the cooking process. Pinene, heated with 50 per cent of sulphur at 200° for 23 hours, gave about 50 per cent of cymene.[6] The light oil obtained by the acid hydrolysis of wood under pressure contains only 4 to 5 per cent of cymene.[7]

In laboratory cooks, the yield of acetic acid varied from 2.6 to 4.2 per cent of the weight of the wood, the average corresponding to one acetyl group per molecule of α-lignin.[8] The formation of formic acid was insignificant, being only 0.04 to 0.09 per cent. Hönig[9] obtained 2.151 to 9.078 grams of volatile acids per liter of sulphite liquor, this being equivalent to 0.72 to 3.03 per cent of the weight of the wood. In three liquors examined, the ratio of acetic to formic acid varied from 5.6:1 to 13.6:1. The occurrence of succinic and protocatechuic acids has also been reported.[10]

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[1] P. Klason and B. N. Segerfelt, C. A., **8** (1914), 1345; H. Bergström, *Papier-Fabr.*, **13** (1915), 229; A. S. Wheeler and C. R. Harris, *J. Am. Chem. Soc.*, **47** (1925), 2836.

[2] P. Klason, *Ber.*, **33** (1900), 2343.

[3] A. W. Schorger, *J. Ind. Eng. Chem.*, **10** (1918), 258–260.

[4] Z. Kertész, *Chem. Ztg.*, **40** (1916), 945–948.

[5] C. F. Cross and A. Engelstad, *J. Soc. Chem. Ind.*, **43** (1924), 255T.

[6] S. Komatsu *et al.*, C. A., **17** (1923), 2577.

[7] E. Heuser *et al.*, *Z. angew. Chem.*, **36** (1923), 37–38.

[8] E. Hägglund and C. B. Björkmann, *Svensk Kem. Tid.*, **36** (1924), 142.

[9] M. Hönig, *Chem. Ztg.*, **36** (1912), 889–890.

[10] W. Buddens, *Papier-Zeit.*, **16** (1891), 1813.

The high acetyl content of hardwoods may be the reason why, in cooking these woods by the sulphite process, it is necessary to use a liquor high in bases. This permits neutralization of the acetic acid which is so readily formed.[1]

The relief gases contain acetaldehyde, acetone, methyl alcohol, acetic and formic acids, and furfural.[2] One thousand liters of sulphite liquor, equivalent to 100 kilograms of pulp, will give:

	Kilograms
Acetaldehyde	0.06
Acetone	0.20
Methyl alcohol	0.53
Ethyl alcohol (by fermentation)	6.32

According to Bergström,[3] 8 to 10 kilograms of methyl alcohol are produced per metric ton of pulp. About 3 kilograms escape in the relief gas. The yields from pine and spruce differ little.

Spent sulphite liquor contains considerable amounts of reducing sugars formed by hydrolysis of hemicelluloses and a portion of the cellulose. In some cases, appreciable quantities of unhydrolyzed carbohydrates may exist in the solution.[4] Krause[5] found the following amounts of sugar:

	Mitscherlich, per cent	Ritter-Kellner, per cent
Total sugars	1.48	1.47
Pentoses	0.47	0.41
Mannose	0.48	0.48
Fructose	0.28	0.25
Galactose	0.01	0.01
Glucose	....	Trace

According to Hägglund,[6] the liquor contains 2.3 per cent of sugar, consisting of:

	Per Cent
Xylose	30.0
Mannose	41.7
Galactose	2.6
Fructose	3.0
Undetermined	22.7

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[1] C. G. Schwalbe and E. Becker, *Z. angew. Chem.*, **32** (1919), 231.

[2] Z. Kertész, *Chem. Ztg.*, **40** (1916), 945.

[3] H. Bergström, *Papier-Fabr.*, **8** (1910), 506; **10** (1912), 677.

[4] E. Oman, *Tecknisk Tids.*, **46** (1916), 6–8.

[5] H. Krause, *Chem. Ind.*, **29** (1906), 217.

[6] E. Hägglund, *Biochem. Z.*, **70** (1915), 416.

It is possible to obtain up to 20 per cent of sugars from the wood without injuring the pulp.[1]

Klason[2] gives the sugar content of sulphite liquor as 3.3 to 3.6 per cent. The composition of the sugars formed is compared with that of the wood in the following table:

	Wood, per cent	Sugars formed based on wood	Per cent
Cellulose	50.0	Glucose	7.9
Hemicelluloses	16.0	Mannose	2.5
Lignin	30.0	Galactose	1.3
Protein	0.7	Arabinose	4.3
Resin and fat	3.3	Xylose	0

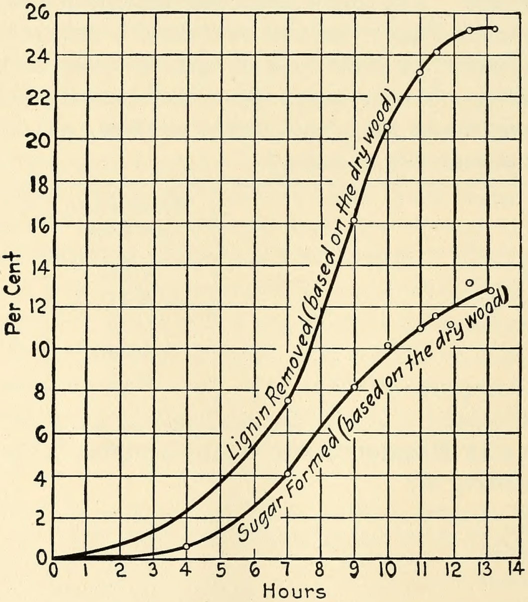

FIG. 8.—Comparison of rate of removal of lignin and formation of sugar in a sulphite cook. (*After Sherrard and Suhm.*)

On fermentation, the maximum yield of alcohol is 1.4 per cent of the volume of the liquor—usually only 1 per cent.

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[1] E. HÄGGLUND, *Svensk Kem. Tid.*, **36** (1924), 292.

[2] P. KLASON, *Papier-Fabr.*, **15** (1917), 641; **16** (1918), 1; *Svensk Papers Tid.*, **20** (1917), 176.

Canadian sulphite liquors contain 0.5 to 1.75 per cent of fermentable sugars.[1] Owing to the higher concentration of sulphur dioxide in the cooking liquors in winter, the spent liquors contain 1.94 to 2.80 per cent of sugar in winter and 1.65 to 2.20 per cent in summer.[2]

The rate of formation of sugars in the Mitscherlich process has been studied by Sherrard and Suhm.[2] The total concentration of sulphur dioxide was 3.8 per cent, of which 2.39 per cent was free and 1.41 per cent combined. The first sugar determination, made at the end of the fourth hour, showed that little sugar was formed below 100°. From this point, the rate of sugar formation increased with the steam pressure to about the seventh hour, and was greatest between the seventh and ninth hours (Fig. 8). At the end of the eleventh hour, the point corresponding with the best quality of pulp, the yield of sugar was 11 per cent. Increasing the total sulphur dioxide to 5.60 per cent, of which 4.46 per cent was free, gave 16 per cent of sugar, but the increase was offset by a corresponding decrease in the yield of pulp. The rate of removal of lignin and the formation of sugar were equal up to the eighth hour, at which point the removal of the lignin became much more rapid. When 90 per cent of the lignin had been removed, the yield of sugar was 12 per cent.

In the quick-cook process, the sugar is formed more rapidly and in greater yield than in the Mitscherlich process.[3] Formation of sugar is rapid at the beginning of the third hour and is completed at the end of the seventh. The usual variations in the quantity of free sulphur dioxide in the digester have no appreciable effect on the quantity of sugars produced, nor do variations between 130 and 150° in the final temperature. Spruce gave about 25 per cent more sugar than jack pine.

Before it can be fermented, the liquor must be neutralized. In addition to sulphur dioxide, which is very toxic to yeast, the solution contains 0.15 to 0.73 per cent of acetic acid, and 0.008

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[1] B. Johnsen and R. W. Hovey, "Utilization of Waste Sulphite Liquor," Dept. Interior, Canada, Forestry Branch, *Bull.*, **66** (1919), 105.

[2] E. C. Sherrard and C. F. Suhm, *J. Ind. Eng. Chem.*, **14** (1922), 931; *cf.* E. Hägglund, "Die Sulfitablauge . . .," p. 18.

[3] E. C. Sherrard and C. F. Suhm, *J. Ind. Eng. Chem.*, **17** (1925), 194; for the cooking conditions see R. N. Miller and W. H. Swanson, *Paper Trade J.*, **78,** 15 (1924), 178.

FORMATION OF SUGARS FROM SPRUCE BY THE QUICK-COOK SULPHITE PROCESS

Cook	Time, hours	Maximum temperature	Sugar on wood, per cent	Yield of pulp, per cent
676	6.5	140°	17.97	46.1
677	6.0	130	18.40	55.0
678	9.0	131	16.82	47.35
680	8.5	130	21.60	48.8
682	6.5	140	17.80	46.0
683	6.5	150	18.26	45.55

to 0.016 per cent of formic acid.[1] Neutralization is partially accomplished with lime and completed by agitation with calcium carbonate. This requires 4 to 5 hours. Complete neutralization with lime produces partial destruction of the sugars and gives an undesirable alkaline reaction. After settling, the clear liquor is fermented at a temperature of 29 to 30°, for 70 to 80 hours, by the addition of beer yeast and nutrients. The yield of alcohol averages 1 per cent by volume.

It is preferable to have the liquor slightly acid. If alkaline, the hydrogen-ion concentration being between 10^{-8} and 10^{-9}, the sugar is split into glycerine and acetaldehyde, thus reducing the yield of alcohol:

$$C_6H_{12}O_6 = C_3H_8O_3 + CO_2 + CH_3.CHO.$$

The acetaldehyde then undergoes the Cannizzaro reaction:

$$2CH_3.CHO + H_2O = C_2H_5OH + CH_3.COOH.$$

The composition of the crude alcohol is given below:

	I, Per cent by weight	II, Per cent by weight	III, Per cent by weight
Strength of alcohol	94.2	94.0	94.5
Methyl alcohol	3.2	0.8	0.35
Acetaldehyde	0.35	1.0	0.00
Fusel oil	0.24	0.7	0.10

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[1] E. HÄGGLUND, "Die Sulfitablauge und ihre Verarbeitung auf Alcohol," Braunschweig (1921), 82 pp.

Acetone is present in very small amount. Acetaldehyde is usually present though the amount is variable. Two samples of the crude alcohol contained 2.61 and 5.48 per cent of acetaldehyde, and 1.28 and 0.54 per cent of paraldehyde.[1] On fractionation, the portion of b.p. 21 to 22° contains 75 per cent of acetaldehyde; that between 22 and 50°, 30 per cent of acetaldehyde besides esters; while the fraction between 50 and 70° contains mainly acetone, 20 per cent of methyl and ethyl alcohols, and small amounts of aldehydes. A fraction, b.p. 101 to 120°, was found to consist of almost pure acetal.[2] The "tails" consist mainly of fusel oil. There have been identified propyl, isobutyl, butyl, and amyl alcohols, and borneol.

Soda Process.—It requires at least 20 per cent of sodium hydroxide to obtain a good pulp. In practice an excess of alkali is used, so that the amount varies from 25 to 35 per cent of the dry weight of the wood. A portion of the black liquor, on account of the free alkali present, is used for the next cook. For every cord of wood in the form of chips, there are used about 900 gallons of sodium hydroxide of a concentration of 6 to 10 per cent. From 1 to 2 hours are required to bring the digester to the cooking temperature, where it is held 4 to 8 hours. Heating is performed by the introduction of steam. The steam pressure varies from 100 to 130 pounds, corresponding to temperatures of 170 to 180°. Circulation within the digester is obtained by releasing the pressure at intervals.

The "black" or spent liquor is evaporated to a sp. gr. of 1.4 to 1.6, incinerated, the ash causticized with lime and reused. Owing to mechanical losses, it is necessary to add about 20 per cent of fresh sodium hydroxide.

The yield of pulp is about 40 per cent. Conifers require more alkali per cord, longer cooking, and give less pulp per cord than hardwoods.[3] Hardwoods are cooked in about 4 hours, while spruce requires 6 to 7 hours. The following data are the result of mill experience:

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[1] E. Heuser *et al.*, *Papier-Fabr.*, **20** (1922), 1–5.

[2] A. W. Owe, *Papier-Fabr.*, **20** (1922), 1564.

[3] J. A. de Cew, *J. Soc. Chem. Ind.*, **26** (1907), 561–563.

Alkali Required and Yield of Pulp

Species	NaOH as Na_2CO_3 pounds	Wood		Pulp	
		Specific gravity	Weight per cord, pounds	Oven-dry, per cent	Air-dry, pounds
Black spruce (*Picea nigra*).....	900	0.41	2,250	40	1,000
Hemlock (*Tsuga canadensis*)...	950	0.42	2,300	38	970
Poplar (*Populus grandidentata*)	800	0.43	2,350	44	1,150
Basswood (*Tilia americana*)...	800	0.425	2,325	44	1,135
White birch (*Betula alba*)......	800	0.58	3,190	42	1,490
Soft maple (*Acer rubrum*)......	850	0.64	3,520	40	1,560
Yellow birch (*Betula lutea*).....	850	0.66	3,630	40	1,610

Aspen may be successfully cooked with 20 to 25 per cent of sodium hydroxide.[1] Yields as high as 56 to 58 per cent can be obtained in a cooking period of 3 to 4 hours.

Digestion of wood with caustic soda in the presence of oxygen lowered the yield of pulp from 41.5 to 38.2 per cent, while the bleach consumption increased from 9.0 to 11.3 per cent of chlorine.[2] Cooking is facilitated by applying a vacuum to the wood in the digester, allowing the cooking liquor to enter, and applying a pressure of 100 to 110 pounds. In this way the air is removed and a very uniform impregnation of the chips is obtained. Rinman[3] claims to improve the yield of cellulose by having a small amount of a catalytic reducing metal, such as mercury, present in the cooking liquor.

During the cooking process, the carbohydrates passing into solution are converted into saccharinic acids, while the lignin is converted into soluble sodium salts. According to Hägglund,[4] Norway spruce gives 42.8 per cent of cellulose, while the waste liquor contains 21.6 per cent lignin, 3.2 per cent acetic acid, 1.7 per cent formic acid, 1.7 per cent methyl alcohol, and 18.2 per cent of oxyacids; of the latter, 55 per cent are present as oxyacids and 45 per cent as lactones. Lactic acid is present to the extent of 0.9 per cent of the weight of the wood.

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[1] H. E. Surface, "Effects of Varying Certain Cooking Conditions in Producing Soda Pulp from Aspen," *U. S. Dept. Agr. Bull.*, **80** (1914).

[2] H. Wallin, C. A., **14** (1920), 3790.

[3] E. L. Rinman, U. S. P. 1319360 (1919); B. N. Segerfelt, *Pulp Paper Mag. Can.*, **19** (1921), 452–453.

[4] E. Hägglund, *Cellulosechemie*, **5** (1924), 81–87.

Pine wood cooked with caustic soda gives:[1]

	Per Cent
Pulp	37.0
Turpentine	0.4
Methyl alcohol	0.5
Fats and resins	0.75
Humus and humic acids	31.00
Soluble humic acid, oxyacids and lactones	20.00
Acetic acid	3.00
Formic acid	3.00

The humus substances may be precipitated by saturating the black liquor with carbon dioxide at 75°, or at proper concentrations, with sodium chloride and other salts. The humic acids are not affected by this treatment, but may be precipitated with acids. The oxyacids contain lactic acid and saccharinic acids.

Bergström[2] cooked wood by the soda process at a pressure of 140 pounds, and obtained the following yields of methyl alcohol based on the dry wood·

	Methyl Alcohol, Per Cent
Spruce (*Picea excelsa*)	0.67
Pine (*Pinus silvestris*)	0.67
Longleaf pine	0.68
Shortleaf pine	0.66
Poplar	0.67
White birch	0.81
Eucalyptus	0.83

The distribution of methoxyl in the products from cooking jack pine (*Pinus divaricata*) with sodium hydroxide has been investigated by Aiyar.[3] Each charge consisted of 45.4 kilograms of wood and 20 per cent of sodium hydroxide having a concentration of 96 grams per liter. The wood contained 4.84 per cent of methoxyl, equivalent to 2.2 kilograms. After the first 2 hours the removal of methoxyl was very slow. Data on the amounts of lignin and methoxyl in the pulps indicate that all the methoxyl is associated with the lignin, and that the methoxyl is combined with the lignin in only one way.

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[1] E. L. Rinman, *Papier-Fabr.*, **10** (1912), 39, 101.

[2] H. Bergström, *Papier-Fabr.*, **11** (1913), 427–428.

[3] S. S. Aiyar, *J. Ind. Eng. Chem.*, **15** (1923), 714–716.

Distribution of Methoxyl in Cooking Jack Pine

Duration of cook from maximum pressure, hours	Yield of pulp, per cent	CH_3O in pulp		CH_3O in black liquor		CH_3O in black liquor	
		Kilograms	Per cent	Kilograms	Per cent	Fixed, kilograms	Volatile, kilograms
−0.5	80.7	1.714	4.67	0.59	0.43	0.22	0.45
0	66.5	1.196	3.96	1.127	0.46	0.84	0.43
+0.5	58.4	0.914	3.45	1.40	0.567	0.64	0.78
1	51.6	0.64	2.74	1.83	0.985	1.27	0.76
2	44.6	0.33	1.60	1.89	0.975	1.50	0.63
3	46.0	0.32	1.52	1.92	1.180	1.64	0.47
4	37.1	0.33	1.95	2.70	0.980	1.64	0.94(?)
6	45.7	0.24	1.19	2.34	0.927	2.26	

A series of soda cooks[1] made on aspen, loblolly pine, and jack pine permits following the changes in the composition of the wood as the cook progresses. The woods were cooked with 20 per cent of their weight of sodium hydroxide at a maximum temperature of 170° over periods of 0.5 to 7 hours. The chips were impregnated with the liquor at a pressure of 100 to 110 pounds per square inch, at 20 to 30°, before cooking. The data show that approximately 90 per cent of the cooking takes place during the first 2 hours. As judged by the chlorine method for determining cellulose, the cellulose is initially removed faster than the lignin. This is due mainly to loss of pentosans. In the case of aspen, the pulp retains uniformly about 8 per cent of very resistant pentosans. Only in the middle of the cook is the lignin removed faster than the cellulose. Most of the acetic and formic acid is produced during the first half hour. The total organic solids in the black liquor reach a maximum at the end of the first 2 hours.

Many attempts have been made to obtain by-products from the black liquor. Destructive distillation of the black liquor from a cord of hardwoods gave 6.9 gallons of a mixture of methyl alcohol and acetone.[1] Rinman[2] mixed the spent liquor with lime and distilled it at a temperature of 400° in the presence of steam. There were obtained per ton of pulp, 400 to 500 kilograms of fuel gas, 100 kilograms of higher alcohols, ketones, hydrocarbons, cresols, etc., and 100 kilograms of a spirit consisting of 50 per cent acetone, 25 per cent methylethyl ketone,

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[1] S. D. Wells *et al.*, *Paper Trade J.*, **76,** 24 (1923), 49–55; M. W. Bray and T. M. Andrews, *Ibid.*, **76,** 19 (1923), 49–51.

DATA ON SODA COOKS

Species	Time of cook, hours	Based on dry wood				Cellulose in pulp, per cent
		Yield of pulp, per cent	Lignin, per cent	Cellulose, per cent	α-Cellulose, per cent	
Aspen	0	100.0	23.4	62.1	43.2	62.1
	0.5	51.5(?)	18.9	57.0	37.3	71.0
	1.5	60.5	4.8	55.0	52.2	91.0
	2	57.5	3.2	53.6	40.8	83.3
	3	55.0	1.4	53.3	41.4	97.0
	4	52.5	0.9	51.0	40.0	97.1
	5	52.0	0.8	50.4	37.0	96.9
	7	49.4	0.7	48.0	39.7	97.4
Loblolly pine	0	100.0	29.7	60.5	24.2(?)	60.5
	0.5	81.4	25.2	52.4	....	64.4
	1.5	70.3	16.6	51.4	....	73.1
	2	61.2	12.2	47.2	....	77.1
	3	49.4	5.3	43.2	25.8	87.5
	4	49.0	4.7	43.2	28.6	88.0
	5	47.8	4.4	44.4	34.3	92.8
	6	41.5	1.9	38.2	25.6	93.1
	7	39.9	1.6	37.4	25.6	93.6
Jack pine	0 *	100.0	32.8	59.8	42.6	59.8
	0.5	80.7	25.6	50.4	16.5(?)	62.5
	1.5	58.4	14.0	43.0	32.6	73.6
	2	51.6	9.0	42.0	35.1	81.5
	3	43.8	3.2	41.0	28.5	93.7
	4	39.9	2.6	37.8	27.4	94.8
	5	37.0	1.0	35.6	29.7	96.4

* Old liquor.

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[1] A. H. WHITE and J. D. RUE, *Met. Chem. Eng.*, **16** (1917), 182–186.

[2] E. L. RINMAN, *Papier-Fabr.*, **10** (1912), 39–41, 101–104.

and 25 per cent of ethyl alcohol. Little methyl alcohol was produced.

Sulphate Process.—The sulphate process differs from the soda process through the presence of a certain amount of sodium sulphide, the sulphur of which is lost for the most part during the cook and the subsequent treatment of the spent liquor. The name is derived from the custom of restoring the sulphur by the addition of sodium sulphate to the black liquor previous to incineration, sodium sulphide being formed by reduction. A modification is the soda-sulphur process, wherein sulphur is added directly to the caustic soda liquor. During cooking some

$$6NaOH + 4S = 2Na_2S + Na_2S_2O_3 + 3H_2O$$

sodium thiosulphate is formed in addition to sodium sulphide. The pulps obtained by the sulphate process and its modification are essentially identical.

The sodium sulphide has a very beneficial effect not only on the strength of the pulp but on the yield as well, which is 10 per cent greater than by the soda process. The function of the sulphur is not completely understood. According to Klason and Segerfelt,[1] the sodium sulphide does not become caustic until the sulphur has entered into combination with the lignin, so that the cellulose is not subjected to as great actual causticity as in the soda process. Arrhenius[2] has determined that the digestion of wood with sodium sulphide, sodium hydroxide, or their mixture, can be expressed as a unimolecular reaction. The incrustants are dissolved 28 times faster than the cellulose at 148°, but only 8.7 times faster at 170°. At 270°, the cellulose and incrustants dissolve at the same rate. With sodium sulphide and sulphate liquors, the lignin is attacked somewhat more rapidly than with caustic soda, while the velocity of attack on the cellulose itself is greatly reduced.

Wells[3] cooked jack pine with 20 per cent of sodium hydroxide and 2 per cent of sulphur at a temperature of 170°. The sulphur accelerated the removal of incrustants and reduced the loss of cellulose during the first half hour, 50 per cent. The papers made from the sulphate pulp showed marked increase in bursting and tensile strength, and in tearing and folding resistance over soda pulp. From a chemical standpoint there is little difference between soda and sulphate pulps.

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[1] P. Klason and B. Segerfelt, *Papier-Fabr.*, **9** (1911), 1093–1099.

[2] S. Arrhenius, *Zellstoff u. Papier*, **4** (1924), 182–184.

[3] S. D. Wells, *Pulp Paper Mag. Can.*, **21** (1923), 623–626.

DATA ON SULPHUR-SODA COOKS

Cook No.	Time to maximum temperature, minutes	Total time of cook, minutes	Based on dry wood				Cellulose in pulp, per cent
			Yield of pulp, per cent	Lignin, per cent	Cellulose, per cent	α-Cellulose, per cent	
Wood	..	...	100.0	32.65	58.9	42.2	58.9
865	40	40	82.75	24.8	54.6	36.3	65.9
866	70	70	63.0	13.5	47.4	35.7	75.2
867	60	105	48.6	4.0	45.8	37.8	94.1
870	60	150	40.55	2.1	38.6	30.0	95.1
868	85	173	43.2	2.5	41.0	32.0	94.9
869	70	246	43.03	2.0	41.6	34.4	96.8

As in the soda process, the carbohydrates are largely converted into oxyacids. Based on the organic matter, the spent liquor has the following composition:[1]

	PER CENT
Lignin	54.29
Resin and fatty acids	2.47
Formic acid	3.69
Acetic acid	5.16
Oxyacid lactones	30.34

Meta- and para-saccharinic acids were identified, though the principal constituent is an isomer of isosaccharinic acid.

The chemicals used in the sulphate process represent about 20 per cent, calculated as sodium hydroxide, of the weight of the wood. The liquor used in the digesters contains 90 to 100 grams of sodium hydroxide, 25 to 30 grams of sodium sulphide, and 10 grams of sodium carbonate per liter. The wood is cooked at a temperature of 150 to 170° for a period of 3 to 6 hours. The yield of pulp varies from 45 to 50 per cent.

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[1] P. KLASON and B. SEGERFELT, *l.c.*

A regenerated soda ash had the following composition:

	Per Cent
Sodium carbonate	61.73
Sodium sulphide	21.50
Sodium sulphite and thiosulphate	7.33
Sodium hydroxide	3.50
Sodium silicate	1.22
Sodium sulphate	2.78
Ferric oxide	0.04
Insoluble and loss	1.90

Of the sulphur originally present as sodium sulphide, 51.8 per cent was combined with the lignin, 15 per cent was obtained as volatile sulphur compounds, principally mercaptan and dimethyl sulphide, and 16.4 per cent was unaccounted for. The volatile sulphur compounds, particularly the mercaptan, have an exceedingly unpleasant odor. Under the same conditions, pine wood gave twice as much mercaptan as spruce. The amount of mercaptan formed can be reduced, and the dimethyl sulphide increased by increasing the amount of alkali, whereby also an easy-bleaching pulp is obtained. In this case, about 100 grams of mercaptan are formed from a ton of dry wood. If the amount of alkali is reduced in order to obtain a kraft pulp, the amount of mercaptan formed may be increased tenfold. During the cooking operations, 20 per cent of the methoxyl groups are split off the lignin as methyl alcohol, mercaptan, and dimethyl sulphide.

The formation of methyl alcohol and its derivatives takes place as follows:[1]

$$\begin{aligned} &R.OCH_3 + NaOH = R.ONa + CH_3OH. \\ &R.OCH_3 + NaSH = R.ONa + CH_3SH. \\ &CH_3SH + NaOH = CH_3SNa + H_2O. \\ &R.OCH_3 + CH_3SNa = R.ONa + (CH_3)_2S. \end{aligned}$$

The non-condensable gases from a digester producing 1375 kilograms of pulp, contained about 20 grams of mercaptan. The condensate contained 2 liters of oil, of which 200 grams was dimethyl sulphide, the remainder turpentine. The condensed water contained 5 kilograms of methyl alcohol smelling strongly of trimethylamine. The black liquor from 16.5 tons of pulp would produce, by destructive distillation, 4.2 kilograms of hydrogen sulphide and 380 kilograms of mercaptan. During incineration to recover the soda, 1.4 kilograms of hydrogen sulphide and 4.5 kilograms of mercaptan escaped combustion and passed out in the chimney gases. The other sulphur losses in the flue gases were 2197 kilograms of sodium sulphite and 278 kilograms of free sulphur dioxide.

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[1] P. Klason, *Wochbl. Papierfabr.*, **39** (1908), 3859–3861, 3963–3966.

According to Falk,[1] the relief condensate from the manufacture of a ton of cellulose from pine wood contains:

	In oil, kilograms	In water, kilograms
Mercaptan	0.062	0.06
Dimethyl sulphide	0.927	0.17
Dimethyl disulphide	0.103	0.05
Turpentine	8.487	0.92
Residue from distillation	0.721	
Methyl alcohol	.....	5.00
Ammonia	.....	0.18

Pine and spruce give about the same amount of crude methyl alcohol.[2] About 13 kilograms of methyl alcohol, containing 0.5 per cent of acetone, are formed in the manufacture of 1000 kilograms of pulp.

None of the numerous methods proposed for disposing of the offensive relief gases is an unqualified success. Schwalbe[3] passes the gases through comminuted wood, which acts as an absorbent or contact substance, the gases being destroyed by oxidation. After losing its efficiency, the wood can be cooked with alkali without producing the odor of mercaptan. The oxidation may be assisted by the use of chlorine or other oxidizing agents. Klason[4] recommends passing the relief gases through efficient condensers, the uncondensed portion being burned in a furnace or absorbed in the concentrated black liquor before it is incinerated. Mercaptan gives with salts of the heavy metals the compound $M''(CH_3S)_2$; however, only the mercaptides of the precious metals are odorless.

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[1] H. Falk, *Papier-Fabr.*, **7** (1909), 469–472.

[2] H. Bergström, *Papier-Fabr.*, **10** (1912), 677–678.

[3] C. G. Schwalbe, *Zellstoff u. Papier*, **1** (1921), 69–72; **2** (1922), 175–178; G. P. 319594 (1917).

[4] P. Klason, *Paper Trade J.*, **79**, 2 (1924), 30–36.

It is difficult to remove the sulphur compounds from the turpentine obtained by the sulphate process so that it will remain odorless on prolonged standing. Agitation with 5 to 10 per cent of 50 per cent sulphuric acid in the cold, until the odor disappears[1], is only a temporary success. The best results are obtained with a solution of bleaching powder.[2] Other oxidizing agents, such as oxides of nitrogen,[3] ultra-violet light in presence of air or oxygen, followed by ferric chloride,[4] have also been proposed. The logical though difficult step is to collect the turpentine before the temperature within the digester is sufficiently high to form organic sulphur compounds.[5] Spruce gives 1 to 1.5 kilograms and pine up to 10 kilograms of turpentine per ton of pulp.[6] When purified, the oil consists mainly of α-pinene and a small amount of β-pinene.

Sodium Sulphite Process.—In recent years, interest in the use of sodium sulphite as a pulping agent has been revived.[7] In the Keebra process, the wood is cooked with about 40 per cent of its weight of sodium sulphite.[8] The spent liquor is incinerated as in the sulphate process, during which principally sodium carbonate, sodium sulphide, and sodium sulphate are formed. Under certain conditions, a large part of the sulphur escapes in the flue gases as sulphur dioxide. The recovered ash is treated with sulphur dioxide, whereby sodium sulphite is reformed.[9] Sodium thiosulphate is also produced, owing to the presence of sodium sulphide.

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[1] P. Klason and H. Person, *Papier-Ztg.*, **32** (1907), 4; **33** (1908), 3779.

[2] B. R. Armour, E. P. 194286 (1923); C. A. Jobson, U. S. P. 1493454 (1924); H. W. Fosse, *Ber. pharm. Ges.*, **25** (1915), 303–313.

[3] A. Luttringer, *Papier-Fabr. Fest u. Auslandsheft*, **12** (1914), 64–67.

[4] H. Dedichen and O. M. Halse, U. S. P. 1253793 (1918).

[5] O. Rodowski, *Paper Trade J.*, **78,** 14 (1924), 75.

[6] O. M. Halse and H. Dedichen, *Ber.*, **50** (1917), 623–630.

[7] W. Clifford, *Paper Ind.*, **3** (1921), 1247; Anon., *Paper Trade J.*, **77,** 10 (1923), 51.

[8] L. Bradley and E. P. McKeefe, Can. P. 219557 (1922).

[9] L. Bradley and E. P. McKeefe, Can. P. 236532 (1923).

The use of neutral sodium sulphite was protected by Cross[1] in 1880, but held as of only theoretical interest.[2] In addition to sodium sulphite,[3] ammonium sulphite,[4] a mixture of sodium sulphite and sodium acetate,[5] and a mixture of sodium sulphite and sodium hydroxide[6] have been suggested.

The Keebra process is unique in the use of a liquor that is nearly neutral, and this accounts for the unusual qualities of the pulps. Little information is available on the exact nature of the cooking process. The reactions involving the removal of the incrusting substances by means of sulphites and alkalis become antagonistic in a mixture of these chemicals. Replacement of 10 per cent of the sodium sulphite with sodium hydroxide greatly retards pulping. This appears to hold up to the point where 80 per cent of the mixture is represented by sodium hydroxide. The results are then similar to the soda process, though there is an improvement in the yield and quality of the pulp.

The yield of pulp from coniferous woods is about the same as by the sulphate process, though about 25 per cent more chemicals are required. The pulp approaches sulphate kraft in strength and is much lighter in color, in which respect it resembles unbleached sulphite. Sodium sulphite gives with hardwoods 20 per cent more pulp than the soda process. The pulp is exceptionally strong, but lacks the softness, opacity, and felting properties of soda pulp.

Minor Pulping Processes.—The use of chlorine for removing lignin has also been revived. The process is essentially the Cross and Bevan laboratory method for determining cellulose. De Vains[7] uses an aqueous solution of chlorine, and Cataldi, gaseous chlorine.[1] The raw material is boiled with alkali before chlorination and the chlorinated derivatives are removed with alkali. According to Cerruti,[2] the preparation of 100 kilograms of dry pulp from poplar by the Cataldi process requires a minimum of 45 kilograms of chlorine and 9 kilograms of sodium hydroxide. Pomilio[3] gives a consumption of 28 kilograms of chlorine and 5 kilograms of sodium hydroxide. The pulp from poplar contains 74 per cent of α-cellulose and 21 per cent of β- and γ-cellulose.

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[1] C. F. Cross, E. P. 4984 (1880).

[2] C. F. Cross and E. J. Bevan, "Paper-Making" (1900), 66.

[3] W. Schacht, G. P. 122171 (1901) and 131118 (1902); *Papier-Ztg.*, **26** (1901), 3143; *Papier-Fabr.*, **54** (1923), 2851.

[4] C. F. Sammet and J. L. Merrill, U. S. P. 1016178 (1912); L. Brech and E. Tyborowski, U. S. P. 1100519 (1914).

[5] M. Müller and O. Heigis, G. P. 284681 (1914); E. P. 156512 (1921).

[6] R. Blitz, F. P. 155014 (1883); L. Bradley, and E. P. McKeefe, Can. P., 246477 (1925).

[7] A. R. de Vains, E. P. 189561 (1921); 198975 (1922).

The use of chlorine gas on straw gives pulps having a high copper number, which reaches 9 in some cases.[4] Waentig[5] considers chlorine gas no more difficult to use than chlorine water. Franz[6] has protected the use of a solution of chlorine in carbon tetrachloride.

Chlorine has been used successfully in pulping the cereal straws, but its application to wood, in the form of chips, is hindered by the difficulty of securing penetration. Waentig and Gierisch[7] boil wood shavings 0.2 to 0.3 millimeter thick with 0.1 per cent sodium hydroxide solution. The shavings are then treated in the cold with chlorine gas for several hours, washed to remove the hydrochloric acid formed, then treated with 1.0 per cent sodium hydroxide solution. Wood in the form of chips must be chlorinated under a pressure of 6 atmospheres.

The most promising procedure consists in giving the wood a preliminary cook with sodium hydroxide or sodium sulphite, so that the wood can be mechanically separated into individual fibers before chlorinating.

The use of phenols,[8] with or without the presence of a mineral acid,[9] is too expensive. The recovery of phenol is low, owing to its condensation with the lignin. The reaction is discussed in detail in the chapter on lignin.

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[1] For a bibliography of the chlorine processes see C. J. West, *Paper Trade J.*, **79,** 14 (1924), 43–44.

[2] C. Cerruti, *Giorn. chim. ind. applicata,* **4** (1922), 64–65.

[3] U. Pomilio, *Chimie & Industrie,* **6** (1921), 267; **8** (1922), 41.

[4] W. Schacht, *Papier-Fabr.,* **21** (1923), 521; **22** (1924), 121.

[5] P. Waentig, *Papier-Fabr.,* **22** (1924), 456.

[6] A. Franz, G. P. 323936 (1919).

[7] P. Waentig and W. Gierisch, *Text. Forsch.,* **2** (1920), 69–79.

[8] F. A. Bühler, *Chem. Ind.,* **26** (1903), 138; *Papier-Ztg.,* **25** (1900), 3256; E. P. 6651 (1898).

[9] R. Hartmuth, G. P. 326705 and 328783 (1919); E. Legeler, *Cellulosechemie,* **4** (1923), 61; C. Claessen, E. P. 160482 (1919).

The use of aliphatic and aromatic amines,[1] and acid chlorides, such as sulphuryl chloride, thionyl chloride, acetyl chloride,[2] etc., is of only general interest. It is stated that lignin can be removed from wood by heating it with concentrated formic or acetic acid, containing 0.3 to 0.7 per cent sulphuric acid, without injuring the cellulose.[3]

Wood cooked with calcium polysulphide[4] is not reduced to a pulp, but is softened sufficiently so that it can be separated into fibers mechanically. The reaction is accompanied by a disagreeable odor exceeding that of the sulphate process.

Wood Pulps.—It is difficult to classify wood pulps on chemical data alone (Tables 1 to 4). Pulps showing nearly identical chemical composition may behave very differently from the standpoint of paper making. Krull[5] has used the terms "hard," "normal," and "soft" to define sulphite pulps. The classification is based on the lignin content, which was determined by treating the moist pulp with hydrogen chloride gas. A hard pulp is one suitable for the manufacture of pergamyn paper, and a soft pulp is particularly suitable for bleaching. A normal pulp has intermediate lignin values and is adapted to the manufacture of ordinary papers.

CLASSIFICATION OF SULPHITE PULPS

Mitscherlich		Ritter-Kellner	
Lignin, per cent	Designation	Lignin, per cent	Designation
6.5–7.0	Hard	7.5–9.5	Hard
5.5–6.0	Normal	6.5–7.5	Normal
5.0–5.5	Soft	4.5–6.5	Soft
1.0–2.0	Bleached		

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[1] W. SCHLOSSER, G. P. 328729 (1919).

[2] R. SCHWARZKOPF, G. P. 328730 (1919).

[3] Akt. Ges. für Zellstoff-u. Papier-Fabr., G. P., 309551 (1916); A. FOULON, *Zellstoff u. Papier*, **5** (1925) 212–213.

[4] A. TINGLE, *Paper*, **34** (1924), 653, 1000; V. DREWSEN, U. S. P. 996225 (1911).

[5] H. KRULL, *Papier-Fabr. Fest u. Auslandsheft*, **19** (1921), 65–70.

TABLE 1.—COMPOSITION OF COMMERCIAL SULPHITE PULPS[1]
(In per cent of dry, ashless pulp)

Number	Kind of pulp	Ash	Copper number	Copper number corrected	Hydrate copper number	Furfural	Pentosan	Neutral wood gum	Methyl CH_3	α-Cellulose
9	Mitscherlich, easy bleaching	0.53	1.94	1.63	0.31	3.12	5.37	....	0.24	90.52
10	Mitscherlich, hard	0.38	2.53	1.95	0.58	2.54	4.36	5.40	0.43	
11	Mitscherlich, extra hard	0.81	2.52	1.83	0.69	....	....	8.60		
12	Mitscherlich, bleachable	0.29	2.11	0.96	1.15	....	....	8.63		
13	Mitscherlich, pergamyn	0.79	2.53	1.76	0.77	3.31	5.69	....	0.27	
15	Mitscherlich, pergamyn	0.63	2.40	1.60	0.80	3.22	5.53	....	0.39	
18	Mitscherlich, pergamyn	1.08	2.41	1.98	0.43	3.44	5.91	....	1.00	87.3
20	Mitscherlich, pergamyn	1.09	1.59	1.26	0.33	3.08	5.30	....	0.78	
22	Mitscherlich, pergamyn	0.97	2.46	2.00	0.46	3.57	6.13	....	0.88	
42	Mitscherlich, bleached	0.41	2.59	1.51	1.08	....	....	8.03	0.07	
24	Ritter-Kellner, unbleached	0.78	2.15	1.93	0.22	....	....	5.87		
26	Ritter-Kellner, bleachable	0.30	2.32	1.94	0.38	3.28	5.63	5.50	0.25	
27	Ritter-Kellner, unbleached, average	0.54	2.13	1.55	0.58	2.71	4.66	4.5		
29	Ritter-Kellner, unbleached	0.48	2.49	1.68	0.81	3.59	6.17	....	0.22	
32	Ritter-Kellner, unbleached	0.45	3.02	2.61	0.41	2.45	4.23	4.23	0.17	90.75
33	Ritter-Kellner, hard, bleached	0.42	3.24	2.64	0.62	....	....	7.48	0.14	
34	Ritter-Kellner, soft, bleached	0.50	3.17	2.53	0.64	2.44	4.18	6.52		
37	Ritter-Kellner, soft, bleached	0.41	3.22	2.42	0.80	2.09	3.59	5.00	....	86.56
46	Purified ("Edel") sulphite	0.46	2.31	1.42	0.89	1.89	3.24	....	0.17	90.56
47	Purified ("Edel") (Norway)	0.35	1.21	0.30	0.91	3.30	5.64	....	0.13	90.32
48	For artificial silk	0.52	2.68	1.85	0.83	3.43	5.87	....	0.12	84.92
52	No. 37 purified with lime	0.18	0.41	0.09	0.32	2.95	5.05	....	0.10	92.81

[1] C. G. SCHWALBE and E. BECKER, *Paper*, **27**, 25 (1921), 22.

TABLE 2.—COMPOSITION OF COMMERCIAL MITSCHERLICH PULPS[1]
(In per cent)

Record number	Description	Wood	Moisture	A soluble in hot water	B soluble in 1 per cent NaOH	B corrected for A	Lignin	Cellulose	α-Cellulose	β-Cellulose	γ-Cellulose
P 176	Unbleached.......	Spruce and balsam	4.9	0.9	10.5	9.6	1.6	96.1	82.1	3.2	13.8
P 188	....	....	3.5	1.6	12.5	10.9	5.2	95.3	82.8	5.1	14.1
P 206	Unbleached.......	Spruce and balsam	4.5	0.6	12.4	11.8	1.3	95.3	86.6	2.1	12.7
P 187	Unbleached.......	Spruce	4.3	1.2	11.4	10.2	7.0	94.6	82.2	3.4	13.9
P 185	Unbleached.......	Spruce	4.4	0.6	9.8	9.2	6.2	94.8	82.8	3.2	13.8
P 186	Unbleached.......	Spruce	3.3	1.7	12.7	11.0	7.8	90.8	83.7	1.4	13.7
P 213	Unbleached.......	Hemlock	4.3	0.5	14.2	13.7	1.4	92.4	83.8	3.3	13.9
P 207	Bleached.........	Spruce and balsam	3.9	0.5	13.9	13.4	0.9	98.4	84.5	4.1	11.6
P 175	Bleached.........	Spruce and balsam	4.6	0.0	11.6	11.6	0.5	97.1	81.4	3.6	13.2

[1] M. W. BRAY and T. M. ANDREWS, *Paper Trade J.*, **76,** 3 (1923), 51.

Table 3.—Composition of Commercial Soda and Sulphate Pulps[1]

Number	Kind of pulp	Ash	Hydrate copper number	Copper number	Copper number corrected	Furfural	Pentosan	Lignin	Methyl, CH_3	α-Cellulose	Cellulose, Cross and Bevan	Extract with		
												Ether	Alcohol	Alcohol-benzene
1	Kraft (Germany)	1.69	1.14	1.24	0.10	8.59*	9.36	4.13	0.21	86.82	.....	0.42	0.90	1.68
2	Kraft (Germany)	0.95	1.19	2.48	1.29	6.59	11.24	7.72	0.18	88.69	.....	0.42	0.40	2.07
3	Kraft (Germany)	....	....	1.20	....	5.48	9.32	....	0.34	.....	95.28	0.24	0.45	
4	Kraft (Norway)	....	....	....	....	5.19	8.82	....	0.42	.....	95.66	0.15	0.59	
5	Soda, unbleached (Germany)	....	....	1.61	....	4.32	7.35	....	0.32	.....	93.44	0.10	0.16	
6	Soda, unbleached (U. S. A.)	....	....	....	....	4.50	7.65	....	0.31	.....	.....	0.25	0.27	
7	Soda, unbleached	0.30	0.39	2.28	1.89	6.17	10.56	6.20	0.41	.....	88.36			
8	Soda, unbleached	1.45	....	....	....	5.01	8.59	....	0.42					
9	Soda, unbleached	1.29	....	....	....	6.53	11.15							
10	Soda, unbleached	0.70	0.45	0.76	0.31	5.13	8.80	2.30	0.20	88.64				
11	Soda, from pine, non-bleachable	1.23	0.83	0.83	....	3.75	6.43							
12	Soda, from aspen, unbleached (U. S. A.)	....	....	0.65	....	8.12	13.63	....	0.18					
13	Soda, easy bleaching	1.25	0.94	0.50	....	3.46	5.94	....	0.44	.....	95.20			
14	Soda, bleached (Germany)	0.70	1.11	2.50	1.39	4.84	8.38	0.58	0.04	85.09	.....	....	0.52	0.64
15	Soda, bleached (Germany)	....	....	3.99	....	3.79	6.45	....	0.07	.....	95.97	0.05	0.24	

* If this furfural value is correct, that for pentosan should be 14.4.

[1] C. G. Schwalbe, *Zellstoff u. Papier*, **2** (1922), 283.

TABLE 4.—COMPOSITION OF SEMICOMMERCIAL PULPS*[1]

Cook number	Process	Bleaching powder, 35 per cent available chlorine	Yields	Moisture	Ash	Cold-water-soluble, 48 hours	Hot-water-soluble, 3 hours	Alkali-soluble, 1 per cent NaOH, 1 hour	Acetic acid by hydrolysis	Ether extract
2	Soda	0	33.8	3.48	0.90	1.27	0.62	2.46	0.06	0.41
		7	32.8	4.94	0.91	0.51	0.08	3.40	0.06	0.52
		15	32.5	5.66	1.22	0.45	0.18	9.81	0.04	0.76
3	Soda	0	42.8	3.91	1.12	0.71	0.26	2.81	0.07	0.49
		12	41.9	6.26	0.92	0.58	1.07	4.93	0.06	1.10
		20	40.7	5.79	0.90	1.27	1.21	6.92	0.04	0.71
4	Sulphate	0	39.0	3.64	1.01	1.23	0.82	2.18	0.06	0.63
		6	38.7	5.74	0.83	0.00	0.00	2.28	0.03	0.89
		15	39.2	5.49	1.21	0.00	0.00	8.51	0.04	0.93
5	Sulphate	0	48.2	4.89	1.16	1.25	0.40	2.62	0.10(?)	1.65
		10	47.6	6.04	1.27	0.59	0.00	3.61	0.04	1.42
		25	46.2	5.97	1.40	1.23	0.91	14.02	0.04	1.10
White spruce wood		....	....	....	0.2	2.3	3.8	8.8	1.6	1.3

Cook number	Process	Pentosan	Methyl-pentosan	Methoxy groups	Cellulose	Lignin (non-cellulose)	In cellulose				
							Alpha	Beta	Gamma	Pentosan	Methyl-pentosan
2	Soda	3.82	1.25	0.47	96.20	2.11	80.30	13.27	6.43	3.42	1.54
		3.98	1.66	0.26	97.16	2.66	55.93	34.22	9.85	3.87	1.88
		4.09	0.63	0.29	97.05	2.22	51.50	37.80	10.70	3.41	1.92
3	Soda	7.77	1.14	0.89	93.17	4.03	85.66	7.81	6.53	7.31	1.52
		8.24	1.18	0.57	94.26	5.86	60.57	34.19	5.24	7.45	1.33
		8.20	1.35	0.32	94.77	4.55	53.01	35.07	11.92	6.80	1.50
4	Sulphate	6.05	1.07	....	96.17	1.88	81.80	10.31	8.07	5.81	1.62
		7.67	1.35	0.24	95.68	3.43	72.20	18.72	9.08	6.95	1.01
		7.17	1.62	0.18	95.40	2.64	62.95	26.90	10.15	6.20	0.97
5	Sulphate	10.04	0.92	0.68	94.56	3.39	84.20	6.31	9.49	9.96	1.29
		10.07	0.64	0.26	94.00	5.53	64.70	23.98	11.32	8.30	1.70
		9.90	0.85	0.25	94.56	4.04	56.87	31.55	11.58	8.46	1.46
White spruce wood		11.9	1.9	5.3	58.6	28.3	63.6	10.4	26.1		

* Results in per cent.

[1] S. D. WELLS, *J. Ind. Eng. Chem.*, **13** (1921), 936.

Hard Mitscherlich pulp is especially suitable for pergamyn. Ritter-Kellner pulp, though less suitable, can also be used for this purpose, as shown by the data below. A pulp for the manufacture of pergamyn should have a high corrected copper number and a low hydrate copper number.

	Lignin, per cent	Copper number corrected	Ash, per cent
Ritter-Kellner, hard	7.79	2.82	0.86
Ritter-Kellner, after beating for 3 hours	....	3.31	2.93
Mitscherlich, hard	6.96	2.51	0.95
Mitscherlich, after beating for 1 hour	....	4.22	1.57
Mitscherlich, after beating for 2.75 hours	....	5.16	1.70

In addition to lignin and normal cellulose, all wood pulps contain varying amounts of pentosans and hexosans; if bleached, also oxycellulose. The methods and results of analyses of various pulps by Lenze[1] are open to question; *e.g.*, the oxycellulose content of unbleached Mitscherlich pulp is given as 15.66 per cent.

Sulphite pulp, free from lignin and ash, has the following composition:[2]

	Per Cent
Cellulose	87.00
Mannan	6.00
Xylan	4.50
Lævulan	2.5

Specially purified pulps had only a trace of mannan, while normal unbleached pulps contained up to 4.18 per cent.[3] The mannan content of bleached Mitscherlich pulp was 0.47 per cent.[4]

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[1] F. Lenze, B. Pleus, and J. Müller, *J. prakt. Chem.*, **101** (1920), 213–264.

[2] E. Hägglund and F. W. Klingstedt, *Cellulosechemie*, **5** (1924), 57.

[3] F. Lenze, B. Pleus, and J. Müller, *J. prakt. Chem.*, **101** (1920), 213–264.

[4] E. Heuser and W. Dammel, *Cellulosechemie*, **5** (1924), 49.

Schwalbe and Becker[1] give chemical analyses of various pulps, from which only general conclusions can be drawn. The bisulphite process removes more pentosans and methoxyl than the alkaline processes. According to Schwalbe,[2] the pentosan content of a pulp is a good indication of the process by which it was manufactured. It would be impossible, however, to state from the pentosan content of a pulp that it had been made by a certain process without knowing the nature of the raw material. A sulphite pulp from a hardwood contains about the same amount of pentosan as a coniferous pulp made by an alkaline cook.

Bleaching reduces the ash and the lignin, and increases the value for wood gum through the formation of oxycellulose and other degradation products. The reducing capacity is also increased accordingly. Wood pulp can be so purified by bleaching, followed by cooking with lime under pressure, that it is very similar to cotton in composition.

Unbleached soda pulp is high in ash, pentosan, and lignin, and low in resin, "wood gum," and reducing substances. Unbleached Mitscherlich pulp is high in ash, resin, lignin, and pentosan, and has a relatively high reducing property; in comparison, Ritter-Kellner pulp has correspondingly lower values.

The strength of kraft pulp, which is made from coniferous woods, is due to the length of the fibers and to mild cooking conditions. The reactions are not sufficiently drastic to remove all of the incrustants, so that the cellulose is not so subject to attack. In the Mitscherlich process, the pulp is washed *in situ* and removed from the digester by hand. This procedure preserves the length of the fibers, which is decreased by blowing the digester. The strength of kraft pulp appears to be due in part also to the presence of resins and fats, which serve as binding agents.[3] The glyceride of linoleic acid is of particular importance, since it is gradually converted into linoxyn by oxidation. The best pulp is obtained from green wood, since in the old, the linoxyn is already largely formed.

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[1] C. G. Schwalbe and E. Becker, *Paper* **27**, 25 (1921), 20.

[2] C. G. Schwalbe, *Z. angew. Chem.*, **31** (1918), 52.

[3] C. G. Schwalbe, *Papier-Fabr. Fest u. Auslandsheft*, **21** (1923), 60; A. Abadie, *Paper Trade J.*, **51,** 6 (1910), 46.

The resin content of various pulps is shown in the following table:[1]

	Ether extract	Alcohol extract	Total extract
Spruce wood	0.60	0.38	0.98
Kraft	0.17	0.43	0.60
Soda, unbleached	0.22	0.20	0.39
Soda, from aspen	0.59	0.76	1.35
Soda, bleached	0.05	0.24	0.29
Mitscherlich, unbleached	0.68	0.31	1.01
Mitscherlich, bleached	0.70	0.52	1.21
Ritter-Kellner, unbleached	0.86	0.49	1.35
Ritter-Kellner, bleached	0.65	0.45	1.11
Nitrating pulp	0.16	0.35	0.51
Nitrating cotton	0.14	0.23	0.37
Pure cotton	0.10	0.20	0.30

The resin from sulphite pulp gives the cholesterol reaction with acetic anhydride and sulphuric acid, while that from soda and sulphate pulps does not.

Hägglund[2] was unable to find any consistent relationship between the mechanical properties of pulps and their chemical constants. It sometimes happens that a well-cooked pulp is as strong or stronger than an undercooked pulp.

The hygroscopic moisture varies with the purity of the pulp, the temperature, and the humidity of the atmosphere. Lespius[3] determined the hygroscopic moisture in various pulps at a temperature of 20° and at a humidity of 55 per cent. The results in the following table are based on the dry weight of the fibers:

	Hygroscopic Moisture, Per Cent
1. Aspen, white mechanical pulp	11.7
2. Spruce, white mechanical pulp	11.94
3. Spruce, brown mechanical pulp	11.71
4. Straw soda pulp, bleached	9.25
5. Wood soda pulp, unbleached	9.40
6. Wood soda pulp, bleached	9.80
7. Wood sulphite pulp, unbleached	10.07

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[1] C. G. Schwalbe, *Z. angew. Chem.*, **31** (1918), 58.

[2] E. Hägglund, *Papier-Fabr.*, **17** (1919), 301.

[3] B. Lespius, *Ber.*, **18** (1885), 2491.

Certain incrustants such as occur in Mitscherlich pulps have a high hygroscopicity.[1] Mitscherlich pulps for pergamyn manufacture are more hygroscopic than cellulose, while Ritter-Kellner pulps are less so.

Discoloration of Sulphite Pulp.—Sulphite pulp on storage, especially in moist air, frequently becomes pink or brown. Muth[2] thought that the discoloration was due to decomposition of tannin in the wood during boiling with sulphite liquor. The same opinion was held by Harpf.[3] Unbleached pulp treated with sodium hydroxide, lime water, and nitric acid gave the same coloration as waste sulphite liquor. Ferric chloride gave a green color with wood and a violet color with sulphite pulp, but no characteristic reaction for tannin could be obtained with the spent liquor. He found that oxidizing agents developed the color and that this could be removed by the use of antichlors or fresh sulphite liquor.

According to Klemm,[4] the coloration is due to reduction of the tannin by sulphur dioxide and its subsequent oxidation. Support for this view was obtained by heating tannin with sulphurous acid, whereby a light-colored solution turning red with oxidizing agents was obtained. On dipping paper into this solution and exposing it to light and air a red coloration developed.

Legrand[5] attributes the coloration to oxidation of residual incrusting substances. The tendency to color is greater the lower the purity of the pulp. Mitscherlich pulp is more susceptible to staining than Ritter-Kellner. The color is apparently not due to tannin but to the oxidation of residual lignin or ligninsulphonic acid.[6] Freshly precipitated ligninsulphonic acids show the same coloration with oxidizing agents as unbleached pulp. The substance actually producing the coloration has not been isolated. A specific preventative agent was found in potassium persulphate. The pulp is agitated with 0.5 per cent of potassium persulphate and an equal weight of sulphuric acid or aluminum sulphate for 8 to 9 hours. The exact nature of the reaction is unknown. The pulp so treated contains the same amount of lignin as the original and is not bleached. Evidently, the lignin is so modified that it is incapable of subsequent reddening.

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[1] C. G. Schwalbe and E. Becker, *Paper*, **27**, 25 (1921), 20.

[2] E. Muth, *Dinglers polytech. J.*, **291** (1894), 235.

[3] A. Harpf, *Wochbl. Papierfabr.*, **26** (1895), 586, 641.

[4] P. Klemm, *Wochbl. Papierfabr.*, **40** (1909), 2882.

[5] Legrand, *Papier-Fabr.*, **9** (1910), 32–33.

[6] E. Heuser and S. Samuelsen, *Papier-Fabr.*, **20** (1922), 1249, 1285, 1321, **22** (1924), 130.

Copper and especially iron, which is usually derived from the limestone, catalyze the oxidation of the impurities and promote the coloration.[1] Impure alum is also effective.[2] Prevention of coloration is obtained by treating the pulp with sulphurous acid or disodium phosphate.

Bleaching.—The bleaching of sulphite pulp with sodium hypochlorite takes place in four stages.[3] In the first stage the consumption of chlorine is very rapid. If the solution is acid, a red compound which is rapidly oxidized is first formed. This coloration is not obtained in an alkaline solution. During the second stage the yellow impurities are gradually oxidized, while in the third there is a slow oxidation of the colored and colorless oxidation products; unless these are completely removed, the pulp becomes yellow on storage. In the last stage, the cellulose itself is attacked, particularly in an acid medium.

The rate of bleaching is slow in alkaline solutions, and in acid solutions increases in proportion to the square of the acidity.[3] A rise of 7° doubles the rate of bleaching. Between wide limits, the rate of bleaching is independent of the concentration of the hypochlorite. Samples bleached at the higher temperatures are whitest on the basis of equal consumption of chlorine. Owing to decomposition of the hypochlorite and oxidation of the cellulose, greater quantities of chlorine are required to produce the same whiteness, the higher the acidity.

The bleaching action at 38° was eight times more rapid than at the ordinary temperature.[4] A higher temperature caused weakening of the fiber. Pulp that is being circulated can be bleached with 40 per cent of the amount of chlorine required for pulp not kept in motion. The cause is incorrectly attributed to the bleaching effect of atmospheric oxygen.

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[1] H. E. Wahlberg, *Papier-Fabr.*, **21** (1923),204–205; **22** (1924), 229–230.

[2] O. L. Berger, *Paper*, **30**, 5 (1922), 16.

[3] J. Nussbaum and W. Ebert, *J. Soc. Chem. Ind.*, **26** (1907), 1063.

[4] C. Beadle and H. P. Stevens, *J. Soc. Chem. Ind.*, **33** (1914), 727–730.

The rate of bleach consumption is a linear function of the logarithm of the time during the main course of the reaction and (probably) within the temperature limits of 0 to 50°. The final color of the pulp is largely independent of the bleaching temperature.[1] The effect of temperature on the time of bleach consumption is shown in the following table:

TIME REQUIRED FOR 90 PER CENT BLEACH CONSUMPTION

Temperature, degrees Centigrade	Total time, minutes	Point of 90 per cent bleach consumption, minutes	Per cent of total time required to reach 90 per cent bleach consumption
21	713	220	30.9
35	220	75	34.2
41	130	50	38.5
46	84	34	40.5

The formation of yellow, stable chloramines[2] does not appear to be a factor in the bleaching of wood pulps, owing to the small amount of nitrogenous compounds present. Hard water is without effect upon the rate of bleaching, color, and yield of bleached pulp.[3] The final color of the pulp is independent of consistencies up to 7 per cent with temperatures ranging from 21 to 46°. The rate of bleach consumption increases with the consistency, this effect being greatest at lower temperatures.[4]

Pulp is ordinarily bleached with a solution of bleaching powder, in its normally alkaline condition, at temperatures of 30 to 40°. An alkaline reaction is superior to an acid one. The best results are obtained by bleaching at the ordinary temperature with two-thirds of the bleach liquor acidified with carbon dioxide, then completing the operation at 30 to 35° with the remaining one-third of ordinary alkaline bleach liquor.[5]

Bleaching experiments conducted in a ball mill at 30 to 35° gave a better yield and quality of pulp in a shorter time than cold bleaching.[1] Passage of a current of air through the apparatus cut the time in half for warm bleaching, but had no influence in the cold. The α-cellulose value was reduced by temperatures above 35° and by prolonged cold bleaching. The effect of air is purely mechanical, since nitrogen had the same effect.[2] Carbon dioxide is formed by the action of hypochlorite solutions on all forms of cellulose. For every gram of active chlorine consumed per 100 grams of cellulose, 0.26 to 0.28 gram of carbon dioxide is produced. This forms calcium bicarbonate with the lime in the bleaching powder. The calcium bicarbonate has a buffer action on the hydrogen-ion concentration, reducing it to a point where the bleaching action comes to a standstill. Removal of the carbon dioxide and dissociation of the bicarbonate are facilitated by agitation, heat, and a current of air.

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[1] C. E. CURRAN and P. K. BAIRD, *Paper Trade J.*, **79,** 11 (1924), 45; G. K. SPENCE, *Tech. Ass. Pulp and Paper Ind.*, Series **4** (1921), 39.

[2] C. F. CROSS, E. J. BEVAN, and J. F. BRIGGS, *J. Soc. Chem. Ind.*, **27** (1908), 260; *Chem. Ztg.*, **32** (1908), 489; R. E. CROWTHER, *J. Soc. Dyers Colourists*, **29** (1913), 38.

[3] C. E. CURRAN and P. K. BAIRD, *Paper Trade J.*, **79,** 3 (1924), 41–43.

[4] C. E. CURRAN and P. K. BAIRD, *Paper Trade J.*, **80,** 16 (1925), 51–53.

[5] V. HOTTENROTH, *Zellstoff u. Papier*, **2** (1922), 6–12.

The normal chlorine consumption may be reduced 45 to 54 per cent if the pulp is treated with chlorine gas, washed with water or preferably sodium hydroxide, and the bleaching completed with bleaching powder.[3] Wells[4] had shown that the bleach consumption could be reduced one-half by conducting the bleaching operation in two stages, with intermediate washing.

Moderate bleaching, as shown by the preparation of test papers, increased the strength of the pulp.[5] According to Frohberg,[6] normal bleaching produces decided loss of strength. The folding test may be reduced 42 per cent and the tensile strength 11 per cent. Overbleaching with 2 per cent excess of bleaching powder gives a soft opaque fiber resembling cotton.

Permanganates are more efficient bleaching agents than bleaching powder. One part of oxygen in the form of potassium permanganate was as effective as 5.5 parts of oxygen in the form of bleaching powder.[7] According to Sutermeister,[8] one part of potassium permanganate produced the same effect as 1.85 parts of calcium hypochlorite; hence the oxygen ratio would be 1:3.6.

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[1] C. G. Schwalbe and H. Wenzl, *Papier-Fabr.*, **20** (1922), 1625–1631.

[2] C. G. Schwalbe and H. Wenzl, *Papier-Fabr.*, **21** (1923), 268, 385; *Z. angew. Chem.*, **36** (1923), 302–304.

[3] E. Heuser and W. Niethammer, *Papier-Fabr. Fest u. Auslandsheft*, **21** (1923), 52–60.

[4] S. D. Wells, *Paper Trade J.*, **71**, 22 (1920), 34; *J. Ind. Eng. Chem.*, **13** (1921), 936.

[5] E. Sutermeister, *Papier-Fabr.*, **12** (1914), 898.

[6] A. Frohberg, *Wochbl. Papierfabr.*, **44** (1913), 3599.

[7] C. Beadle and H. P. Stevens, *J. Soc. Chem. Ind.*, **33** (1914), 727.

[8] E. Sutermeister, *l.c.*

The discoloration of bleached pulps may be due to residual chlorinated and oxidized lignin derivatives, and to oxycellulose. Bachelder[1] heated samples of pulp at 30, 70, 75, 87, and 102°, for 16 hours. Unbleached sulphite and sulphate pulps showed little change of color, while pronounced colorations were obtained with unbleached soda pulp from aspen, and bleached sulphite pulps.

According to Cross and Bevan,[2] the non-cellulose constituents are first chlorinated, while beyond a certain point there is hydrolysis and oxidation of the cellulose. The contention that the cellulose molecule is chlorinated should be accepted with reserve.

The inorganic and organic chlorine present in bleached sulphite pulps has been determined by Schwalbe.[3] The discoloration of bleached pulps is attributed to oxycellulose rather than to organic chlorine compounds, as held by Cross and Bevan.

CHLORINE CONTENT OF BLEACHED PULPS

Bleaching agent	Ash, per cent	Chlorine in ash, per cent	Organic chlorine, per cent	Total chlorine, per cent
$Ca(OCl_2)$	0.83	0.011	0.058	0.069
$Ca(OCl)_2$, double quantity	1.35	0.014	0.053	0.068
NaOCl	0.47	0.012	0.071	0.083
NaOCl, double quantity	0.80	0.055	0.059	0.114
$Ca(OCl)_2$, acid	0.36	0.014	0.052	0.066
$Ca(OCl)_2$, acid, double quantity	0.48	0.008	0.067	0.075
NaOCl, acid	0.37	0.002	0.049	0.051
NaOCl, acid, double quantity	0.68	0.006	0.047	0.053
Unbleached pulp	0.60	.....	0.012	0.012
Commercial bleached pulp	0.99	0.011	0.042	0.053

The writer has examined bleached sulphite pulp, purified by a special process, that contained oxycellulose yet did not turn yellow on prolonged heating at 70°.

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[1] C. L. Bachelder, *Paper*, **24** (1919), 1096–1097.

[2] C. F. Cross and E. J. Bevan, *J. Soc. Chem. Ind.*, **9** (1890), 450; *Chem. Ztg.*, **32** (1908) 489.

[3] C. G. Schwalbe, *Z. angew. Chem.*, **21**(1908), 302–303.

CHAPTER XIII

THE DISTILLATION OF CELLULOSE AND WOOD

Cellulose is profoundly changed by prolonged heating at moderate temperatures. Cotton[1] placed over steam pipes for some months carbonizes completely at a temperature of 120 to 130°. Knecht[2] observed that bleached cotton exposed on watch glasses at a temperature of 93° turned grayish brown after a few days with the formation of oxycellulose. Heated in sealed tubes, the cotton took up oxygen and decreased 50 per cent in strength.

Cellulose heated with water at 340° for about 12 hours is changed, with the evolution of carbon dioxide, into a substance resembling soft coal.[3] The reaction takes place approximately as follows:

$$4C_6H_{10}O_5 = C_{21}H_{16}O_2 + 3CO_2 + 12H_2O.$$

If cellulose is heated with benzene under pressure at 250 to 260°, it gradually decomposes, but with only a slight evolution of gas, to dark-brown, tar-like products, soluble in the benzene.[4]

Destructive Distillation of Cellulose.—Subjected to destructive distillation, cellulose shows an exothermic reaction, though this is not marked if the distillation is sufficiently slow. Chorley and Ramsay[5] claimed an exothermic reaction with raw cotton but not with the purified product (absorbent cotton); however, the data show with the latter a rise of 23° within the retort compared with 54° for jute. The purest cotton obtainable has been observed[1] to give a marked and sudden evolution of heat at 345°.

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[1] C. Koechlin, *Bull. Mulhouse*, **58** (1888), 547.

[2] E. Knecht, *J. Soc. Dyers Colourists*, **36** (1920), 195–198.

[3] F. Bergius, *J. Soc. Chem. Ind.*, **32** (1913), 462; S. Stein, *Chem. Zentr.*, 72, II (1901), 950.

[4] F. Fischer and W. Schneider, C. A., **14** (1920), 2081.

[5] J. C. Chorley and W. Ramsay, *J. Soc. Chem. Ind.*, **11** (1892), 873.

The evolution of water from heated cellulose is most marked at about 290° and the exothermic reaction would be anticipated at this point. In fact, Bantlin[2] found that with cellulose the exothermic reaction took place between 250 and 300°. On heating cellulose up to 1000° over a period of 80 hours, the evolution of water took place as follows:[3]

Temperature, degrees Centigrade	Water, per cent	Temperature, degrees Centigrade	Water, per cent
190	0.43	420	2.42
240	1.57	510	1.94
290	22.61	600	1.03
350	6.57	1,000	0.0
		Total...........	36.57

Only one-half as much water is obtained by rapid as by slow distillation.

Distillations of cotton and wood celluloses, prepared by the sulphite process, have been made by Klason[4] and his associates, with the following results:

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[1] H. Hollings and J. W. Cobb, *J. Chem. Soc.*, **107** (1915), 1110.

[2] G. Bantlin, *J. Gasbel.*, **57** (1914), 32, 55.

[3] O. Rau and G. Lambris, *J. Gasbel.*, **56** (1913), 561.

[4] P. Klason, G. von Heidenstam, and E. Norlin, *Z. angew. Chem.*, **22** (1909), 1205–1214.

	Cellulose from				
	Cotton, per cent	*Pinus silvestris*, per cent	*Picea excelsa*, per cent	*Betula alba*, per cent	*Fagus silvatica*, per cent
Composition of raw material:					
Water	4.82	5.60	6.44	6.65	7.81
Ash	0.13	0.44	0.49	0.92	0.77
Organic matter	95.05	93.96	93.07	92.43	91.42
Distillation products:					
Charcoal	38.82	36.93	34.86	33.39	32.91
Carbon dioxide	10.35	12.83	11.94	11.14	11.96
Ethylene	0.17	0.21	0.19	0.41	0.25
Carbon monoxide	4.15	3.40	3.92	3.49	3.80
Methane	0.27	0.27	0.22	0.47	0.39
Methyl alcohol	.....	Trace	0.07	.....	0.19
Acetone	0.07	0.08	0.13	0.15	0.26
Acetic acid	1.39	2.18	2.79	3.89	3.50
Organic matter in $CH_3.COONa$	5.14	4.22	8.50	7.72	8.67
Tar	4.18	4.85	6.28	9.58	5.23
Water	34.52	34.17	29.99	29.35	31.88
Loss	0.94	0.86	1.11	0.40	0.93

The decomposition of the various celluloses is quite similar. The small amounts of methyl alcohol obtained from the wood celluloses, without doubt, had their origin in residual methoxyl groups. Cotton does not give methyl alcohol, though the presence of 0.277 per cent of methoxyl in absorbent cotton has been reported.[1] The wood celluloses, particularly hardwood, gave markedly greater yields of acetic acid than cotton. This may be due to the higher hemicellulose content; Bergström,[2]

	Cellulose	Starch	Sugar
Acetic acid, per cent	3.28	5.29	8.78

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[1] L. F. Hawley and S. S. Aiyar, *J. Ind. Eng. Chem.*, **14** (1922), 1055.

[2] H. Bergström, *Papier-Fabr.*, **11** (1913), 759.

however, obtained only 0.29 per cent of acetic acid by the distillation of birch "wood gum." The results obtained by Bantlin[1] on distilling cellulose, starch, and sugar indicate that the yield of acetic acid decreases with the increase in molecular complexity of the carbohydrate.

The distillate obtained from filter paper has been examined by Erdmann and Schaefer.[2] They used a kilogram of paper per charge and completed the distillation in 2 hours. The gas contained by volume: 65.5 per cent of carbon monoxide; 19.0 per cent of methane; 11.5 per cent of hydrogen; 2.4 per cent of nitrogen; 0.9 per cent of oxygen; 0.5 per cent of hydrocarbons; and only 0.2 per cent of carbon dioxide. The aqueous distillate contained acetone, formaldehyde, furfural, hydroxymethylfurfural, maltol, and γ-valerolactone.

Filter paper distilled with superheated steam gave 2.5 to 2.8 per cent of acetic acid but no methyl alcohol.[3]

Cotton distilled with or without zinc gave acetone, methylethyl ketone, furan, α-methylfuran, 2,5-dimethylfuran, trimethylfuran, tetramethylfuran, phenol, cresol, acetic acid, traces of toluene, and a compound, $C_{12}H_{14}O$, possibly hydrodiphenyleneoxide.[4]

Diacetyl[5] is also formed. Phenol was the only phenolic constituent found by Wichelhaus[6] in the distillate from 20 kilograms of pure cotton.

Maltol has not been reported as present in wood distillates, though Cross and Bevan[7] obtained it by the incipient roasting of cellulose and lignocellulose, and suggest that the pyrone ring may be represented in the constitutional formula of cellulose. Maltol is a crystalline compound, m.p. 159°, readily soluble in water and giving a violet color with ferric chloride. It is formed in the roasting of malt,[8] and occurs naturally in the needles of white fir (*Abies alba* Mill.)[1] and larch bark.[2] It is identical with the larixic acid of Stenhouse.[3] An isomaltol,[4] m.p. 98°, has been isolated from bread and various roasted food products. It is probably β-methyl-β'-hydroxy-γ-pyrone, while maltol is α-methyl-β-hydroxy-γ-pyrone.[5]

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[1] G. Bantlin, *l.c.*

[2] E. Erdmann and C. Schaefer, *Ber.*, **43** (1910), 2398.

[3] G. Büttner and H. Wislicenus, *J. prakt. Chem.*, **79** (1909), 177.

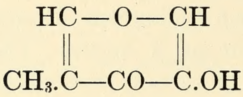
[4] J. Sarasin, *Arch. sci. phys. nat.*, [IV] **46** (1918), 5.

[5] J. M. Johlin, *J. Am. Chem. Soc.*, **37** (1915), 892.

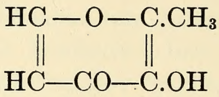
[6] H. Wichelhaus, *Ber.*, **43** (1910), 2922.

[7] C. F. Cross and E. J. Bevan, *J. Soc. Dyers Colourists*, **32** (1916), 135.

[8] J. Brand, *Ber.*, **27** (1894), 806; H. Kiliani and M. Bazlen, *Ibid.*, 3115.



Isomaltol



Maltol

Vacuum Distillation of Cellulose.—In 1918, Pictet and Sarasin[6] reported the interesting discovery that when cellulose or starch is distilled *in vacuo*, *l*-glucosan is obtained in a yield of 45 per cent. At a pressure of 12 to 15 millimeters, a thick yellow oil is obtained, from which *l*-glucosan can be crystallized by the use of acetone; white crystals, m.p. 179.5°; $[\alpha]_D = -66.25°$; triacetate, m.p. 110°; and tribenzoate, m.p. 199.5°. Lævoglucosan has the formula $C_6H_{10}O_5$, contains three hydroxyl groups, and is an anhydride of glucose. Complete hydrolysis with dilute acids at normal pressure requires about 6 hours, and glucose is the only sugar obtained.

Since cellulose gives furan derivatives on destructive distillation, and especially since *l*-glucosan gave ω-brommethylfurfural with hydrobromic acid, Pictet and Sarasin[1] concluded that both cellulose and *l*-glucosan contain the furan ring, and that cellulose is a polymeride of *l*-glucosan. It was then observed that, while ordinary glucose (α-glucose) gave only traces of *l*-glucosan, the latter could be obtained in quantity from many natural β-glucosides;[7] also that when glucose is heated at 150 to 155° at a pressure of 15 millimeters glucosan (α-glucosan) is obtained.[1] Glucosan has the m.p. 108 to 109°, and is *d*-rotatory; $[\alpha]_D = +69.8°$.

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[1] W. Feurstein, *Ber.*, **34** (1901), 1804.

[2] A. Peratoner and A. Tamburello, *Ber.*, **36** (1903), 3407.

[3] J. Stenhouse, *Ann.*, **123** (1862), 191.

[4] A. Backe, *Compt. rend.*, **150** (1910), 78, 540.

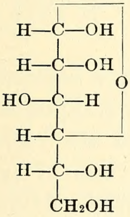
[5] A. Peratoner and A. Tamburello, *Chem. Zentr.*, **76**, II (1905), 680.

[6] A. Pictet and J. Sarasin, *Compt. rend.*, **166** (1918), 38–39; *Helvetica Chim. Acta*, **1** (1918), 87–96; J. Sarasin, *Arch. sci. phys. nat.*, [IV] **46** (1918), 5–32.

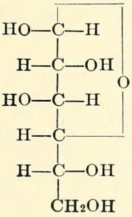
[7] A. Pictet and H. Goudet, *Helvetica Chim. Acta*, **2** (1919), 698.

With the idea that the configuration of the glucose might have a bearing on the glucosan obtained, Karrer[2] distilled β-glucose and, in fact, obtained almost the same yield of *l*-glucosan as from starch. This observation strongly indicated that the β-glucosidal linkage exists in starch and cellulose and that *l*-glucosan and glucosan are formed from β- and α-glucose respectively.

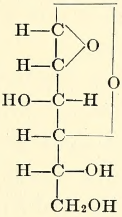
Pictet[3] then derived the two glucosans by dehydration of Böeseken's[4] formulæ for α- and β-glucose. Pictet's formula for *l*-glucosan has been confirmed by Irvine and Oldham,[5] who proved it to be 1, 6-β-glucose anhydride. A different structure was suggested by them for glucosan, though the correctness of the Pictet formula is rendered highly probable by the work of Cramer and Cox.[6]



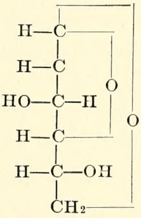
α-Glucose



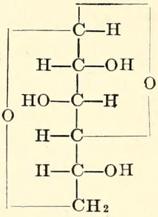
β-Glucose



Glucosan
(α-Glucosan)



(α-Glucosan)
(*Irvine*)



Lævoglucosan
(β-Glucosan)

Irvine and Oldham[5] showed conclusively that there was no structural relationship between *l*-glucosan and cellulose, since they yield entirely different trimethylglucoses. They suggest the expressions α-glucosan and β-glucosan, though the term β-glucosan had been previously substituted for *l*-glucosan by Vongerichten and Müller.[1]

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[1] A. Pictet and P. Castan, *Compt. rend.*, **171** (1920), 243; *Helvetica Chim. Acta*, **3** (1920), 645.

[2] P. Karrer, *Helvetica Chim. Acta.*, **3** (1920), 258.

[3] A. Pictet, *Helvetica Chim. Acta*, **3** (1920), 649; A. Pictet and M. Cramer, *Ibid.*, 640.

[4] J. Böeseken, *Ber.*, **46** (1913), 2612.

[5] J. C. Irvine and J. W. H. Oldham, *J. Chem. Soc.*, **119** (1921), 1744–1759.

[6] M. Cramer and E. H. Cox, *Helvetica Chim. Acta.*, **5** (1922), 884.

When heated in a vacuum and under pressure, especially in the presence of zinc chloride and platinum black, both glucosan and *l*-glucosan undergo various degrees of polymerization. Di-, tetra-, hexa-, and octa-*l*-glucosans,[2] and di- and tetra-glucosans,[3] have been obtained. Tetra-α- and tetra-β-glucosans are easily and completely acetylated or methylated.[4]

Distillation of ethylcellulose *in vacuo* gave only a small amount of oil and no derivative of glucosan.[5] Reilly,[6] working with methylcelluloses containing 25.3 to 43.7 per cent methoxyl, obtained a product corresponding to dimethylglucosan from a methylcellulose containing 28.1 per cent methoxyl. It gave a dimethylglucose on hydrolysis.

A high yield of *l*-glucosan is dependent upon a pure cellulose and rapid distillation. The removal from cotton of compounds soluble in water, alkali, and acid greatly improves the yield. The highest yield obtained by Venn[7] from cotton was 37 per cent, while 40 per cent was obtained from hydrocellulose. Irvine and Oldham[8] distilled 4300 grams of starch, obtaining 1670 grams of syrup, from which 230 grams of pure *l*-glucosan was obtained. During the distillation, acids are formed that hydrolyze the starch and cellulose to β-glucose, which dehydrates and passes over as *l*-glucosan.

In connection with the occurrence of maltol in fir needles and larch bark, it is of interest that *l*-glucosan was first obtained from the glucosides of conifers.[9]

Destructive Distillation of Wood.—The oldest process by which wood was transformed into products of economic value by chemical reactions, is wood distillation. This is not surprising, since a knowledge of the combustibility of wood must have been forced upon the attention of prehistoric man. There naturally followed in the course of ages the observation that limited combustion produced tar and pyroligneous acid in addition to charcoal.

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[1] E. Vongerichten and F. Müller, *Ber.*, **39** (1906), 241.

[2] A. Pictet and J. H. Ross, *Helvetica Chim. Acta*, **5** (1922), 876–883.

[3] A. and J. Pictet, *Helvetica Chim. Acta*, **4** (1921), 788–795.

[4] H. Pringsheim and K. Schmalz, *Ber.*, **55** (1922), 3001–3007.

[5] K. Hess and W. Wittelsbach, *Z. Elektrochem.*, **26** (1920), 237.

[6] J. Reilly, *Helvetica Chim. Acta*, **4** (1921), 616–621.

[7] H. J. P. Venn, *J. Textile Inst.*, **15** (1924), 414.

[8] J. C. Irvine and J. W. H. Oldham, *l.c.*

[9] C. Tanret, *Compt. rend.*, **119** (1894), 158.

The distillation industry uses both hardwoods and softwoods, the most suitable species available being selected. The hardwoods are especially valuable for their high yields of acetic acid and methyl alcohol. Softwoods, on the other hand, give low yields of acetic acid and methyl alcohol, but produce turpentine and tars of special value; hence, unless the charcoal is of primary importance, only the most resinous species are utilized.

Hardwood is usually distilled by heating it in the form of cord wood or short blocks in closed retorts. The distillate settles into two layers, the upper consisting of pyroligneous acid and the lower of tar. This settled tar contains some acetic acid and methyl alcohol that are recovered by distilling the tar with steam. The pyroligneous acid contains the "soluble tar." This is separated as a residue by distillation, the distillate consisting essentially of acetic acid and methyl alcohol. After neutralizing the distillate with lime, the solution is distilled to remove the methyl alcohol, calcium acetate remaining in the still.

Longleaf and Cuban pines are the only native conifers distilled on a large scale. The procedure is similar to hardwood distillation. The methyl alcohol and acetic acid are not recovered, except under special conditions. The tar, owing to the presence of terpenes and decomposition products of resin, floats on the pyroligneous acid. The crude tar is refined by distillation and treatment with chemicals into "wood turpentine," pine oil, tar, tar oils, and pitch. Pitch is obtained directly from the retort towards the end of the distillation and as a residue from the distillation of the tar.

The extraction process as applied to resinous woods involves no chemical reactions. The comminuted wood is distilled with steam to remove the turpentine and pine oil, and then digested with a special gasoline to remove the rosin. The solvent is recovered by distillation and reused.

The data obtained in the distillation of wood should always be interpreted in the light of the experimental conditions as the results may vary greatly according to:

1. Species, dimensions, and moisture content of the wood.
2. Speed and temperature during distillation.
3. Method of heating.

The first systematic investigations on wood distillation were conducted by Violette.[1] Wood, in the form of cylinders 6 centimeters long and 1 centimeter in diameter, was treated with superheated steam, the distillation temperature being measured within the retort near the egress of the steam and distillation products. Owing to the uniform heating of the charge, the yield of charcoal was greatly increased. Violette was primarily interested in obtaining charcoal suitable for gunpowder, hence little attention was paid to the distillate. He found that carbonization took place at about 250°; at 300° "red" charcoal, and at 350° black charcoal were formed. His results should be distinguished from those obtained under industrial conditions where most of the heat is supplied externally.

Under ordinary conditions of distillation, the charcoal retains the structure of the wood. Violette[2] observed that when heated to 300 to 400° in an entirely closed vessel, the wood seemed to melt and flow. When cold it formed a structureless, black, glistening mass, like tar, which contained 67 per cent of carbon and 27 per cent of oxygen. According to Petzholdt,[3] the product resembles coal.

It has been observed that wood becomes very plastic under pressure when heated at 200 to 250°, temperatures below the carbonization point.

Exothermic Reaction.—The distillation of wood is accompanied by a violent exothermic reaction at a temperature of about 275°, as was first noted by Chorley and Ramsay.[4] The increase in temperature due to the exothermic reaction was 30° with oak, 55° with beech, and 40° with alder. According to

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[1] H. Violette, *Compt. rend.*, **26** (1848), 683–685; **27** (1848), 53–55, 55–56; **32** (1851), 713–717; **38** (1854), 107–116; *Ann. chim. phys.*, [3] **23** (1848), 475–508; [3] **32** (1851), 304–350; [3] **39** (1853), 291–342.

[2] H. Violette, *Compt. rend.*, **32** (1851), 715; *Ann. chim. phys.*, [3] **32** (1851), 326.

[3] A. Petzholdt, "Beitrag zur Kenntnis der Steinkohlenbildung," Leipzig (1882), p. 11; cited by E. Donath, *Chem. Ztg.*, **32** (1908), 1272.

[4] J. C. Chorley and W. Ramsay, *J. Soc. Chem. Ind.*, **11** (1892), 395–403, 872–874.

Hornsey[1], when the heat is withdrawn, the exothermic reaction produces a rise of 83° with chestnut and 136° with pine wood.[2]

The thermochemistry of wood distillation has been fully investigated by Klason.[3] Distillation begins at 250°, becomes rapid at about 275°, and is completed at 350°. The following table gives the data obtained for birch wood.[4]

THERMOCHEMISTRY OF THE DISTILLATION OF BIRCH WOOD FOR 8 HOURS AT ORDINARY PRESSURE

Products	Per cent by weight	Heat of combustion, Calories		Heat absorbed by products at 275°
		Per kilogram	On per cent of product	
Charcoal	30.85	7,860	2,428.3	20.1
Tar	16.94	6,053	1,025	40.2
Acetic acid	6.77	3,500	237	14.3
Formic acid	0.61	1,341	8.2	1.4
Methyl alcohol	1.49	5,310	79.1	5.8
Acetone	0.20	7,300	14.6	1.1
Formaldehyde	1.00	4,566	45.7	5.6
Carbon dioxide	10.17	......	....	6.1
Carbon monoxide	3.57	2,430	86.8	2.4
Methane	0.98	13,060	128	1.8
Ethylene	0.25	11,860	29.6	0.3
Volatile oils	3.00	7,875	236.3	7.1
Organic matter, undetermined	3.69	8,598	317.3	8.8
Water	20.48	......	....	147.5
Sum	100.00	......	4,636.4	262.5
Birch wood	......	4,895	....	100.6

All results are calculated for 1 kilogram of wood at the exothermic temperature, 275°. Since the heat of combustion of birch wood is 4895 Calories, and 100.6 Calories are required to bring it to a temperature of 275°, the total heat represented would be 4995.6 Calories. The same calculations on the distillation products represent $4636.4 + 262.5 = 4898.9$ Calories. The total heat set free would be 96.7 Calories.

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[1] J. W. HORNSEY, *J. Soc. Chem. Ind.*, **30** (1911), 730.

[2] Probably degrees Fahrenheit.

[3] P. KLASON, G. VON HEIDENSTAM, and E. NORLIN, *Arkiv Kemi, Mineral. Geol.*, **3** [10] (1908), 1–17; *Z. angew. Chem.*, **22** (1909), 1205; **23** (1910), 1252; *Ullmann's Enzykl. Techn. Chem.*, **6** (1919), 438.

[4] P. KLASON, *J. prakt. Chem.*, **90** (1914), 439.

$$4995.6 - 4898.9 = 96.7 \text{ Calories.}$$

The heat of reaction, however, would be

$$4895 - 4636.4 = 258.6 \text{ Calories.}$$

Similar data[1] for various woods and celluloses are given below:

Thermochemistry of the Distillation of Wood and Cellulose

Substance	Heat of combustion, Calories	Heat of combustion of products, Calories	Heat taken up by products, Calories	Heat liberated, Calories	Heat liberated as per cent of heat of combustion of substance, per cent
Cotton	4,188	3,840.9	288.1	152.3	3.6
Pine wood	5,070	4,605.6	241.1	316.6	6.3
Pine cellulose	4,170	3,854.6	280.1	158.6	3.8
Spruce wood	4,910	4,547.2	233.0	223.3	4.6
Spruce cellulose	4,300	3,896.8	262.9	233.6	5.4
Birch wood	4,910	4,470.4	243.6	289.3	5.9
Birch cellulose	4,550	4,135.5	278.2	239.8	5.3
Beech wood	4,790	4,322.5	245.3	315.5	6.6
Beech cellulose	4,350	3,902.5	281.7	279.1	6.4

Calorific Value.—The calorific values of wood given by Klason in the above table may be supplemented by those of other investigators (p. 439). Most of the early work is unreliable, due to the use of the method based on the reduction of litharge to lead, or to failure to correct for hygroscopic water.

Very complete information on the course of wood distillation, with respect to the formation of primary and secondary products, and the exothermic reaction, was obtained by Klason,[1] by first

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[1] P. Klason *et al.*, *Z. angew. Chem.*, **23** (1910), 1256.

[2] P. Klason, *J. prakt. Chem.*, **90** (1914), 445.

Calorific Values of European Woods[1]

Species	Calories
Oak (*Quercus pedunculata*)	4,620
Ash (*Fraxinus excelsior*)	4,711
Hornbeam (*Carpinus betulus*)	4,728
Beech (*Fagus silvatica*), 60 years old	4,766
Beech (*Fagus silvatica*), 130 years old	4,785
Beech (*Fagus silvatica*), 100 years old	4,770
Birch (*Betula alba*)	4,771
Scotch pine (*Pinus silvestris*)	5,035

[1] E. Gottlieb, *J. prakt. Chem.*, **136** (1883), 392.

Calorific Values of American Woods

Species	Calories*	
Chestnut	4,632	1
Chestnut, leached	4,661	
Pine	4,920	2
Oak	4,764	
Hickory	4,704	
Cherry	4,801	
Birch	4,710	
Poplar	4,811	

* To obtain B.t.u. per pound, multiply the values given in calories in the above tables by 1.796.

[1] H. C. Sherman and C. G. Amend, *School Mines Quart.*, **33** (1911), 30.

[2] S. W. Parr and C. N. Davidson, *J. Ind. Eng. Chem.*, **14** (1922), 935.

conducting the distillation in a cathode light vacuum and then gradually increasing the pressure to atmospheric. The yield and composition of the tar obtained with a high vacuum differed greatly from that at ordinary pressure. The exothermic reaction was found to be due to a secondary decomposition of the tar or pitch, and is not related to the primary decomposition of the wood. Under a high vacuum the pitch distills also, the decomposition of the wood taking place approximately as follows:

$$\underset{\text{Wood}}{2C_{42}H_{60}O_{28}} \rightarrow \left|\begin{array}{l}
\underset{\substack{\text{Primary}\\ \text{charcoal}\\ 20.8\%}}{3C_{10}H_5O} + \underset{16.8\%}{19H_2O} + \underset{6.5\%}{3CO_2} + \underset{4.1\%}{3CO} \\
+ \underset{7.5\%}{2.5CH_3.COOH} + \underset{2.2\%}{H.COOH} + \underset{1.6\%}{CH_3OH} \\
+ \underset{\substack{\text{Pitch}\\ 36\%}}{C_{36}H_{43}O_{16}} + \underset{\substack{\text{Formaldehyde, oils, etc}\\ 4.5\%}}{C_5H_8O}.
\end{array}\right.$$

By distillation under normal pressure over a period of 14 days, the pitch decomposes as indicated below:

$$\underset{\substack{\text{Pitch}\\ 36\%}}{C_{36}H_{43}O_{16}} \rightarrow \underset{\substack{\text{Secondary}\\ \text{charcoal}\\ 21.1\%}}{C_{30}H_{20}O_3} + \underset{8\%}{9H_2O} + \underset{4.3\%}{2CO_2} + \underset{\substack{\text{Oils}\\ 2.8\%}}{C_4H_9}.$$

When the distillation was prolonged to 14 days at atmospheric pressure, the yield of tar was reduced to 1.8 per cent. Under ordinary commercial conditions the yield of tar is about 10 per cent. The variation in the yield of tar under various pressures and distillation periods greatly influences the thermochemistry of the reaction. In the distillation of birch wood[1] there was absorption of heat at the low pressure.

THERMOCHEMISTRY OF CARBONIZATION OF BIRCH WOOD FOR VARIOUS TIMES AND PRESSURES, FINAL TEMPERATURE 400°

	5-millimeter mercury vacuum	Ordinary pressure for	
		8 hours	14 days
Heat of reaction, Calories	+123.1	+258.6	+340.9
In per cent of heat of combustion of wood	+ 2.6	+ 5.3	+ 7.1
Heat liberated, Calories	− 47.6	+ 96.7	+169.2
In per cent of heat of combustion of wood	− 1.0	+ 2.0	+ 3.5

On theoretical grounds, the heat generated by the exothermic reaction should be nearly sufficient to accomplish the distillation without the aid of external heat. This end is approached most nearly by the Stafford[2] process. Hot, dry comminuted wood is fed continuously into the top of a vertical retort and charcoal is removed from the bottom. No external heat is applied to the retort after the process is under way.

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[1] P. KLASON, *l.c.*, 442.

[2] O. F. STAFFORD, U. S. P. 1380262 (1921); *Chem. and Met. Eng.*, **28** (1923), 441.

Experiments on vacuum distillation have also been made by Aschan.[1] Birch distilled at 6 to 8 millimeters gave 6.9 per cent of acetic acid, which is about the normal yield. Acetone apparently was not formed and its occurrence in the usual distillates must be due to decomposition of acetic acid. The yield of charcoal was 45 per cent in comparison with the normal 33 per cent. Similar distillations were made on pine and fir.[2] The charcoals from the three species were almost identical. The conifers gave more formic acid than acetic acid, while the reverse was true of the hardwoods.

The distillation of resinous woods *in vacuo* greatly improves the yield of turpentine.[3]

The presence of *l*-glucosan in the distillate obtained from the distillation of wood under reduced pressure might be expected from the patent of Pictet;[4] Sarasin,[5] however, states that it could not be obtained from wood.

Yields of Products.—The table on page 442 shows the yields of products obtained by Klason[6] and his associates for European species.

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[1] O. Aschan, *Brennstoff-Chemie*, **2** (1921), 273; **4** (1923), 164.

[2] O. Aschan, *Brennstoff-Chemie*, **4** (1923), 129, 145.

[3] M. Adams and C. Hilton, *J. Ind. Eng. Chem.*, **6** (1915), 378–382.

[4] A. Pictet, U.S.P. 1437615 (1922).

[5] J. Sarasin, *Arch. sci. phys. nat.*, [IV] **46** (1918), 32.

[6] P. Klason *et al., Z. angew. Chem.*, **23** (1910), 1252.

YIELDS OF PRODUCTS BY THE DISTILLATION OF EUROPEAN WOODS

	Species			
	Pine, per cent	Spruce, per cent	Birch, per cent	Beech, per cent
Composition of raw material:				
Water	7.52	9.27	8.79	7.11
Ash	0.21	0.22	0.38	0.43
Organic matter	92.27	90.51	90.83	92.46
Distillation products:				
Charcoal	37.83	37.81	31.80	34.97
Carbon dioxide	10.13	10.30	9.96	10.90
Ethylene	0.23	0.20	0.19	0.20
Carbon monoxide	3.74	3.76	3.32	4.22
Methane	0.59	0.62	0.54	0.47
Methyl alcohol	0.88	0.96	1.60	2.07
Acetone	0.18	0.20	0.19	0.20
Methyl acetate	0.01	0.02	0.02	0.03
Acetic acid	3.50	3.19	7.08	6.04
Organic matter in $CH_3.COONa$	8.03	7.75	8.15	5.89
Tar	11.79	8.08	7.93	8.11
Water	22.27	25.70	27.81	26.58
Loss	0.82	1.41	1.41	0.32

An extensive series of investigations on American hardwoods has been made by Hawley and Palmer.[1] The yields may be accepted as comparable to those obtained on an industrial scale.

The portion of the tree from which the wood is taken is of influence, though there is no regularity between species. In general, the yields of acetic acid and methyl alcohol are greater from heartwood than from sapwood, tupelo, however, being a striking exception. The high yield of acetic acid from beech slabs is due to the sapwood. Maple bark gives almost the same yield of methyl alcohol as the slabwood and heartwood.

Senff[2] obtained the best yields of valuable products from sound trunk wood; limbs, decayed wood, and bark were inferior.

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[1] L. F. HAWLEY and R. C. PALMER, *U. S. Dept. Agr. Bull.*, **129** (1914), and **508** (1917).

[2] M. SENFF, *Ber.*, **18** (1885), 60.

In the case of chestnut, Borghensani[1] found that the yields of both acetic acid and methyl alcohol increased in the order: trunk, root, and branch.

YIELDS OF PRODUCTS FROM HEARTWOOD OF VARIOUS SPECIES[2]

Species	Locality	Methyl alcohol, per cent	Acetic acid, per cent	Charcoal, per cent	Tar, per cent
Beech	Indiana	1.95	5.56	43.1	9.7
Beech	Pennsylvania	2.23	5.77	40.6	9.1
Birch	Wisconsin	1.45	6.71	39.0	9.6
Birch	Pennsylvania	1.62	6.19	36.4	12.6
Maple	Wisconsin	1.94	5.42	39.8	12.4
Maple	Pennsylvania	1.94	5.66	40.2	12.5
Red gum	Missouri	1.76	5.70	36.8	11.7
Chestnut	New Jersey	0.90	5.50	47.6	4.7
Hickory	Indiana	2.08	5.05	37.7	13.0
White oak	Indiana	1.34	4.97	49.5	6.3
White oak	Arkansas	1.33	4.23	42.0	9.3
Tupelo	Missouri	1.56	4.49	45.9	11.4
White elm	Pennsylvania	2.12	6.39	40.0	12.1
Slippery elm	Wisconsin	2.03	5.77	40.7	9.6
Silver maple	Wisconsin	1.69	6.30	41.2	12.1
Green, blue, and yellow ash	Tennessee Missouri	1.91	4.64	41.0	11.3
Black ash	Wisconsin	1.79	5.65	38.2	11.4
Chestnut oak	Tennessee	1.22	4.88	39.6	10.2
Tanbark oak	California	1.72	6.89	37.6	9.0
Swamp oak	Louisiana	1.50	4.90	46.5	7.3
Eucalyptus	California	1.33	4.58	48.2	3.7

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[1] G. BORGHENSANI, *Chem. Ztg.*, **34** (1910), 609.

[2] L. F. HAWLEY and R. C. PALMER, *l.c.*

YIELDS OF PRODUCTS FROM SLABWOOD OF VARIOUS SPECIES[1]

Species	Locality	Methyl alcohol, per cent	Acetic acid, per cent	Charcoal, per cent	Tar, per cent
Beech	Indiana	1.79	6.18	39.4	10.6
Beech	Pennsylvania	2.09	6.21	42.3	10.9
Birch	Wisconsin	1.55	6.88	38.1	8.5
Birch	Pennsylvania	1.59	6.10	38.6	10.3
Maple	Wisconsin	1.91	5.11	44.9	9.2
Maple	Pennsylvania	1.78	5.44	37.6	12.3
Red gum	Missouri	1.73	5.23	47.4	7.5
Chestnut	New Jersey	0.87	5.26	52.9	3.7
White oak	Indiana	1.33	4.77	50.5	4.6
White oak	Arkansas	1.46	4.35	46.2	8.7
Tupelo	Missouri	1.86	8.19	46.1	12.1
White elm	Pennsylvania	1.68	6.61	39.7	11.1
Slippery elm	Wisconsin	1.79	5.53	44.0	7.0
Silver maple	Wisconsin	1.77	5.31	44.6	8.0
Green, blue, and yellow ash	Tennessee Missouri	1.43	4.14	45.8	7.9
Black ash	Wisconsin	2.04	5.16	40.5	9.1
Chestnut oak	Tennessee	1.30	4.91	46.9	8.8
Tanbark oak	California	1.53	6.01	41.9	10.0
Swamp oak	Louisiana	1.31	5.43	47.4	8.9
Eucalyptus	California	1.68	5.31	44.2	8.8

YIELDS OF PRODUCTS FROM LIMBS AND BARK OF VARIOUS SPECIES[1]

Species	Locality	Form	Methyl alcohol	Acetic acid
Beech	Indiana	Bark	1.25	2.98
Maple	Wisconsin	Bark	1.88	3.15
Beech	Indiana	Sapwood	1.97	6.67
Chestnut	New Jersey	Limbs	0.96	6.42
Tupelo	Missouri	Limbs	1.64	5.64
Green ash	Missouri	Limbs	2.02	4.51
Tanbark oak	California	Limbs	1.66	
Black oak	California	Limbs	....	6.76

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[1] L. F. HAWLEY and R. C. PALMER, *l.c.*

The softwoods have been studied sparingly in comparison with the hardwoods. The following data were obtained by Adams and Hilton.[1] Each charge consisted of 25 kilograms of wood. The distillation was conducted under diminished pressure until the temperature of the retort reached 250°.

Species	Pyroligneous acid, liters	Methyl, alcohol, per cent	Acetic acid, per cent	Tar, liters	Charcoal	
					Kilos	Per cent
Sugar pine..........	9.8	0.52	2.6	1.26	3.64	14.56
Western yellow pine..	12.4	0.55	2.2	2.09	4.32	17.28
Red fir..............	11.1	0.48	1.8	1.78	5.03	20.12
Silver fir............	10.1	0.51	2.1	1.23	4.77	19.08

Distillation with Superheated Steam.—Following Violette,[2] various attempts have been made to use superheated steam for distilling wood. This heating medium is claimed[3] to give higher yields of methyl alcohol and acetic acid, the latter attaining about 8 per cent with birch. The initial action of the steam is without doubt hydrolytic, most of the acetic acid being formed by hydrolysis of the acetyl groups. According to Büttner and Wislicenus,[4] decomposition of wood with superheated steam begins at 240°. Less methyl alcohol was obtained from birch than by the usual methods, but the yield of acetic acid was much higher, namely, about 10 per cent. Both lignin and cellulose gave acetic acid, but no methyl alcohol was obtained from cellulose.

Effect of Moisture.—The amount of water present in wood influences the character of the distillate, though no general conclusions can be drawn, since the results vary with the species. Palmer and Cloukey[5] distilled beech, yellow birch, and maple which had been seasoned for periods of 18 months, and 4 to 5 months. It is unfortunate that there was not greater variation in the moisture content of the wood, this ranging from 65 to 100 per cent (based on the dry weight). Moisture had a favorable effect on the yield of acetic acid with controlled distillations. In the case of beech, the highest yields of methyl alcohol and acetic acid were obtained by controlling the distillation of the wetter wood. Moisture had little influence on the yield of acetic acid from yellow birch, though a controlled distillation of the drier wood gave the most alcohol. Maple resembled birch in its behavior. The largest yield of formic acid was obtained by the rapid distillation of wet wood, particularly beech.

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[1] M. Adams and C. Hilton, *J. Ind. Eng. Chem.*, **6** (1914), 378; *cf.* H. K. Benson and M. Darrin, *Ibid.*, **7** (1915), 916.

[2] H. Violette, *l.c.*

[3] P. Poore, E. P. 131006 (1919).

[4] G. Büttner and H. Wislicenus, *J. prakt. Chem.*, **10** (1918), 177–234.

[5] R. C. Palmer and H. Cloukey, *J. Ind. Eng. Chem.*, **10** (1918), 262–264.

Order of Formation of Products.—The order in which the various distillation products are formed is of interest. Palmer[1] made a series of distillations, interrupted at definite points, on yellow birch, and found that, aside from gas, formic acid was the first to appear, followed by acetic acid, tar soluble in pyroligneous acid, methyl alcohol, and "settled tar." Birch,[2] containing about 10 per cent of water, gave 8 to 10 per cent of its total acetic acid and 1 per cent of its methyl alcohol before the exothermic reaction set in. According to Blacher,[3] when the distillation is conducted at a temperature not exceeding 260°, about 33 per cent of the normal amount of acetic acid is obtained, and 80 per cent up to a temperature of 300°.

Klason[4] found that the yields of methyl alcohol and acetic acid remained practically constant, regardless of the speed of distillation, under pressures varying from a high vacuum to atmospheric pressure. No acetone was produced *in vacuo*. It is formed at the expense of the acetic acid during a prolonged distillation. The highest yields of formic acid are obtained by vacuum distillation and the lowest by prolonged distillation at normal pressure. The same is true of formaldehyde except that the decrease is less. Klason obtained 1.27 per cent of formaldehyde by vacuum distillation and 0.80 per cent by a distillation at atmospheric pressure lasting 14 days.

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[1] R. C. Palmer, *J. Ind. Eng. Chem.*, **10** (1918), 260–262.

[2] L. F. Hawley and R. C. Palmer, *U. S. Dept. Agr. Bull.*, **129** (1914), 5.

[3] C. Blacher, *Chem. Ind.*, **23** (1910), 508.

[4] P. Klason, *J. prakt. Chem.*, **90** (1914), 413.

The distribution of acetic acid during the slow distillation of the trunk wood of pine was determined by Bornstein.[1] A charge consisted of 1 kilogram of wood containing 3.21 per cent of moisture.

	Pyroligneous acid, grams	Acetic acid, grams
To 250°	65.0	0.91
250–300	65.3	3.32
300–350	145.7	15.15
350–400	71.2	5.48
400–450	20.9	0.48
Total................	.....	25.34 = 2.5 per cent

Non-combustible gases were obtained at 165°, water at 180°, combustible gases at 280°, the first tar at 300°, and sulphur compounds at about 280°.

Pressure above Atmospheric.—Palmer[2] has studied the effect of distilling wood at high pressures. He used pressures mainly up to 150 pounds per square inch and a final temperature of about 335°. At a pressure of 450 pounds, the exothermic reaction was very violent. Pressure produced a slight increase of methyl alcohol, an increase of charcoal and gas, and a decrease of acetic acid and tar. The effect of pressures up to 60 pounds was much greater than for higher pressures, particularly on the tar. At 60 pounds' pressure, the yield of tar was decreased 60 to 65 per cent.

Temperature Control.—We have seen that wood is not decomposed appreciably below 250° and that at 275° an exothermic reaction takes place that may become violent. To avoid loss of methyl alcohol and acetic acid by secondary reactions, it is very essential that the main decomposition be controlled by heating slowly or reducing the external heat at the critical point.

Prior to the discovery of the exothermic reaction, Senff[3] made some small-scale distillations by slow and rapid heating. Slow distillation gave greater yields of acetic acid than rapid.

[1] E. Bornstein, *J. Gasbel.*, **49** (1906), 648.

[2] R. C. Palmer, *J. Ind. Eng. Chem.*, **6** (1914), 890.

[3] M. Senff, *Ber.*, **18** (1885), 60–64.

Species		Total distillate, per cent	Tar, per cent	Acetic acid, per cent	Charcoal, per cent	Gas, per cent
Alder (*Alnus glutinosa* L.)........	*a*	50.53	6.39	5.77	31.56	17.91
	b	47.76	7.06	4.13	21.11	31.13
Birch (*Betula alba* L.)............	*a*	51.05	5.46	5.63	29.24	19.71
	b	42.98	3.24	4.43	21.46	35.56
Oak (*Quercus robur* L.)...........	*a*	48.15	3.70	4.08	34.68	17.17
	b	45.24	3.20	3.44	27.73	27.03
Fir (*Pinus abies* L.)..............	*a*	45.37	4.42	2.73	30.27	24.36
	b	51.75	9.77	2.39	24.18	24.07
Larch (*Pinus larix* L.)...........	*a*	51.61	9.30	2.69	26.74	21.65
	b	43.77	5.58	2.06	24.06	32.17

a. Slow distillation. *b.* Rapid distillation.

Somewhat similar experiments were made under Rudnew.[1] Sawdust (20 to 47 grams) dried at 120° was distilled in a glass retort heated by a metal bath. After reaching 150°, the temperature of the bath was raised 1° per minute to 300°; then the distillation was completed without temperature measurements. It was concluded that most of the acetic acid came from the lignin and that, since linden gave the highest yield, the actual hardness of the wood was not the important factor. The yields of acid are suspiciously high.

	Linden	Birch	Aspen	Oak	Pine	Fir	Birch cellulose	Pine cellulose
Acetic acid, per cent.	10.24	9.52	8.06	7.92	5.65	5.24	6.21	5.07

Barillot,[2] as a result of distillations made on a laboratory (100 kilograms) and on a commercial scale, found that it was necessary to distil slowly and regularly in order to obtain maximum yields of acetic acid, methyl alcohol, and charcoal. Similar conclusions were reached by Borghensani,[3] whose data are given below:

[1] W. Rudnew, *Dinglers polytech. J.*, **264** (1887), 88–92.

[2] E. Barillot, *Compt. rend.*, **122** (1896), 467–471, 735–736.

[3] E. Borghensani, *Chem. Ztg.*, **34** (1910), 609–610.

EFFECT OF RATE OF DISTILLATION ON YIELDS OF PRODUCTS FROM CHESTNUT

Wood			Rate of distillation	Charcoal, per cent	Tar, per cent	Acetic acid, per cent	Methyl alcohol, per cent	Acetone, per cent	Gas, per cent
Bark, per cent	Water, per cent	Form							
5.45	33.17	Trunk	Slow	30.09	3.96	2.70	0.68	0.07	13.20
			Rapid	25.74	3.30	2.25	0.56	0.06	23.19
20.00	17.37	Branch	Slow	22.84	4.32	4.65	1.16	0.12	19.00
			Rapid	19.54	3.60	3.90	0.97	0.11	27.96
20.10	31.14	Root	Slow	26.25	4.06	3.30	0.83	0.08	17.50
			Rapid	22.74	3.38	2.75	0.69	0.07	26.59

The rate of distillation was measured by the weight of distillate collected in a given time (0.5 kilogram per hour by slow distillation), rapid distillation being 20 times faster than slow distillation. In this case the rate had very slight influence on the formation of acetone.

The beneficial effects of temperature control have been strikingly brought out by Palmer.[1] Some of the results are given in the following table:

INFLUENCE OF TEMPERATURE CONTROL ON THE YIELDS OF METHYL ALCOHOL AND ACETIC ACID

Species	Methyl alcohol		Acetic acid	
	Uncontrolled, per cent	Controlled, per cent	Uncontrolled, per cent	Controlled, per cent
Maple	1.56	2.16	5.29	6.30
Maple	1.59	2.36	5.74	5.45
Maple	1.62	2.41	5.91	5.52
Mean	1.59	2.31	5.65	5.76
Beech	2.01	2.15	5.70	6.28
Beech	2.03	....	5.78	
Beech	2.07	....	5.85	
Mean	2.04	2.15	5.77	6.28
Birch	1.59	1.73	6.58	6.96
Birch	1.67	1.76	6.50	6.78
Mean	1.63	1.75	6.54	6.87

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[1] R. C. PALMER, *J. Ind. Eng. Chem.*, **7** (1915), 663.

In all experiments, a final temperature of 350° was reached. The heating bath was so regulated in the controlled runs that the temperature at the center of the retort did not exceed 275 to 300° during the critical period. The various species were not equally benefited by controlled distillations. The increased yield of methyl alcohol was 45 per cent for maple, 6 per cent for beech, and 7 per cent for birch, while the increase in acetic acid for these species was 2, 9, and 5 per cent respectively.

The critical point for methyl alcohol is just before the formation of the tar,[1] but regardless of how the distillation is made, the yield of methyl alcohol falls far short of what would be expected from the methoxyl content of the wood. This is shown in the following table:[2]

	Birch	Maple	Western larch
Methyl alcohol, per cent..............	1.53	1.94	0.65
Methoxyl, per cent..................	6.07	7.25	4.95

The low yields of methyl alcohol are due mainly to the formation of phenol ethers and methane.

Use of Catalyzers.—Various attempts have been made to increase the yields of methyl alcohol and acetic acid by having various added chemicals present during the distillation. The claim[3] for increased yields by distilling wood with sulphuric acid could not be confirmed by Palmer.[4] He found that no methyl alcohol was formed and that the yields of acetic and formic acids were greatly reduced.

The presence of phosphoric acid was beneficial. Palmer[4] used from 1.25 to 23.75 per cent of phosphoric acid, and pressures from 0 to 110 pounds. In one experiment, beech distilled with 2.45 per cent of phosphoric acid at 110 pounds' pressure gave 13.85 per cent of acetic acid. With both beech and maple, there was a pronounced increase in the yield of methyl alcohol, but, in general, the yield of acetic acid was not improved. When tar was distilled with wood, under pressure, in the presence of phosphoric acid, the yield of methyl alcohol was greatly increased, owing to fission of the methoxyl groups in the tar; at atmospheric pressure, no increase was obtained. The most pronounced effect of phosphoric acid was to decrease the soluble tar and reduce the settled tar to a negligible quantity.

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[1] R. C. Palmer, *J. Ind. Eng. Chem.*, **10** (1918), 260.

[2] A. W. Schorger, *J. Ind. Eng. Chem.*, **9** (1917), 566.

[3] Orljavacer Chem. Fabrik, F. P. 357432 (1905); G. P. 185934 (1905).

[4] R. C. Palmer, *J. Ind. Eng. Chem.*, **10** (1918), 264; U. S. P. 1259277 (1918).

On continuing this work, Hawley[1] found that phosphoric acid in concentrations of 0.5 to 1.5 per cent gave a slight decrease of methyl alcohol and a slight increase of acetic acid.

Other chemicals used by Hawley[2] were lime, calcium carbonate, sodium carbonate, sodium silicate, magnesium oxide, ferric oxide, and magnesium chloride. The most promising results were obtained with low concentrations of sodium carbonate.[3] The chemical must be uniformly distributed throughout the wood. Maple with 1.5 per cent and white oak with 0.5 per cent sodium carbonate gave a large increase of methyl alcohol without materially affecting the yield of acetic acid. The yields were:

	Methyl alcohol, per cent	Acetic acid, per cent
Silver maple:		
Untreated	1.61	5.22
Treated	2.39	5.26
White oak:		
Untreated	1.17	4.91
Treated	2.58	5.09

Distillation of cellulose and wood with 20 to 80 per cent of sodium hydroxide increased the yield of gas and tar.[4] Zinc chloride, apparently due to its dehydrating action on the wood, reduced the yield of tar and greatly increased the amount of charcoal.

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[1] L. F. Hawley, *J. Ind. Eng. Chem.*, **14** (1922), 43.

[2] L. F. Hawley, *l.c.*

[3] L. F. Hawley, U. S. P. 1363730 (1920).

[4] F. Fischer and H. Niggemann, *Abhandl. Kennt. Kohle*, **1** (1917), 176–183.

Fremy,[1] in 1835, distilled sugar, starch, and gum with eight parts of lime and obtained a mixture of ketones consisting mainly of acetone.[2] Basset[3] states that wood slowly distilled with only 2.5 parts of lime gave 26 per cent of acetone and higher ketones. With a smaller quantity of lime (0.6 part), Hawley[4] obtained a marked decrease in the yield of acetic acid without an increase of acetone. Basset's results could not be confirmed by Schorger,[5] who obtained about 2 per cent of acetone.

When maple wood is distilled with sodium carbonate, the increased yield of methyl alcohol is at the expense of the methoxyl groups in the charcoal and dissolved tar.[6] The increase, in the case of oak, can be balanced only by taking into consideration the decrease in methane in the gas. It will be noted that only about 70 per cent of the original methoxyl is accounted for in the table below.

DISTRIBUTION OF METHOXYL GROUPS IN THE PRODUCTS OF THE DISTILLATION OF MAPLE AND OAK WOOD

Product	Maple[a]		White oak[b]	
	Blank, per cent	1 per cent Na_2CO_3, per cent	Blank, per cent	1 per cent Na_2CO_3, per cent
Pyroligneous acid	1.62	1.92	1.16	1.84
Dissolved tar	0.34	0.21	0.22	0.16
Settled tar	0.52	0.59	0.46	0.60
Charcoal	0.28	0.04	0.70	0.13
Gas (CH_4 calculated as CH_3O)	1.31	1.47	1.34	0.78
Total methoxyl	4.07	4.23	3.88	3.51

a. Original maple had 6.09 per cent CH_3O. *b.* Original oak had 5.12 per cent CH_3O.

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[1] E. FREMY, *Ann.*, **15** (1835) 277; *Ann. chim. phys.*, [2] **59** (1835), 5.

[2] Contrary to several statements, Fremy does not mention having used wood; nor does he give any yields of acetone.

[3] H. P. BASSET, *Chem. Met. Eng.*, **20** (1919), 190.

[4] L. F. HAWLEY, *l.c.*

[5] A. W. SCHORGER, *J. Ind. Eng. Chem.*, **17** (1925), 944.

[6] L. F. HAWLEY and S. S. AIYAR, *J. Ind. Eng. Chem.*, **14** (1922), 1056.

It would be of interest to determine the effect of the natural mineral constituents of the wood on the distillation products. It is possible that some of the variations usually attributed to a difference in the composition of the lignocelluloses, especially where the same species has grown on different soils, may be due to the effects of the ash.

Charcoal.—The yield and the composition of charcoal depend upon the species of wood, and upon the rate and temperature of distillation. Violette,[1] using steam, obtained the following yields:

YIELDS OF CHARCOAL AT VARIOUS TEMPERATURES

Temperature, degrees Centigrade.	160	170	180	190	200	210	230	250	270	280	300	320	340	350	432	1023	1100	1250
Yield, per cent	98	94.55	88.59	81.99	77.10	73.14	55.37	49.67	37.14	36.16	33.61	32.23	31.53	29.66	18.87	18.75	18.40	17.94

Rapid distillation at 432° gave only 8.96 per cent of charcoal in comparison with 18.87 per cent by slow distillation.

The influence of temperature on the composition[2] of the charcoals is shown below. The ash may be obtained by subtracting

COMPOSITION OF CHARCOALS MADE AT VARIOUS TEMPERATURES

Temperature, degrees Centigrade	Composition, per cent			Temperature, degrees Centigrade	Composition, per cent		
	C	H	O + N		C	H	O + N
150	47.5	6.1	46.3	260	67.9	5.0	26.5
160	47.6	6.1	46.3	270	70.5	4.6	24.2
170	47.8	6.2	46.0	280	72.6	4.7	22.1
180	48.9	5.8	45.1	290	72.5	5.0	22.0
190	50.6	5.1	44.1	300	73.2	4.3	22.0
200	51.8	4.0	44.0	310	73.6	3.8	21.8
210	53.4	4.9	41.5	320	73.6	4.8	21.1
220	54.6	4.2	41.4	330	73.6	4.6	21.3
230	57.1	5.5	37.0	340	75.2	4.4	20.0
240	61.3	5.5	32.7	350	76.6	4.1	18.4
250	65.6	4.8	29.0	432	81.6	2.0	15.2

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[1] H. VIOLETTE, *Ann. chim. phys.*, [3] **32** (1851), 311.

[2] H. VIOLETTE, *Ann. chim. phys.*, [3] **32** (1851), 322.

the sum of the constituents from 100. The residues from heating at temperatures below 270° are very incompletely decomposed.

The following table given by Klason[1] shows the effect of higher temperatures on the yield and composition of the charcoal.

YIELD AND COMPOSITION OF CHARCOAL AT VARIOUS TEMPERATURES

Temperature, degrees Centigrade	Composition, per cent			Yield, per cent
	C	H	O	
200	52.3	6.3	41.4	91.8
250	70.6	5.2	24.2	65.2
300	73.2	4.9	21.9	51.4
400	82.7	3.8	13.5	37.8
500	89.6	3.1	6.7	33.0
600	92.6	2.6	5.2	31.0
700	93.7	2.4	4.8	28.7
800	95.8	1.0	3.3	26.7
900	96.1	0.7	3.2	26.6
1000	96.6	0.5	2.9	26.5

Rinman[2] passed nitrogen over coniferous charcoal heated to 800°. Analysis of the gas evolved indicated that the charcoal had the following composition:

	C	CO_2	CO	CH_4	H
Per cent...............	87.0	5.1	5.3	1.9	0.7

Wood charcoal contains 0.2 to 0.3 per cent of methoxyl,[3] as shown by the Zeisel method. It has been found, also, that methyl alcohol[4] is formed when charcoal is heated at high temperatures, especially above 730°.

The specific gravity of the charcoal examined by Werther[5] varied from 1.45 to 1.53. Pickles[6] obtained the following values:

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[1] P. KLASON, "Ullmann's Enzykl. Techn. Chem.," **6** (1919), 443.

[2] L. RINMAN, *Dinglers polytech. J.*, **246** (1882), 472.

[3] L. F. HAWLEY and S. S. AIYAR, *J. Ind. Eng. Chem.*, **14** (1922), 1056.

[4] L. F. HAWLEY, *J. Ind. Eng. Chem.*, **15** (1923), 697.

[5] G. WERTHER, *J. prakt. Chem.*, **61** (1854), 21.

[6] A. PICKLES, *Chem. News*, **121** (1920), 1.

Source	Density	
	Apparent	Real
Almond	0.48	1.70
Birch chips	0.23	1.44
Birch dust	0.21	1.47
Coconut	0.63	1.71

Charcoal,[1] after treatment with chlorine at a red heat,[1] had a specific gravity of 1.57 to 1.88. If the wood is subjected to great pressure during distillation, the apparent density is greatly increased.[2]

The heat of wetting of charcoal varies from 4.06 to 4.16 calories per gram.[3]

The specific heat of pressed, powdered beech-wood charcoal at various temperatures has been determined by Kunz.[3] Weber[3] found the specific heat at lower temperatures to be:

Temperature, degrees Centigrade	Specific heat	Temperature, degrees Centigrade	Specific heat
435	0.243	1059	0.362
561	0.290	1197	0.378
728	0.328	1297	0.381
925	0.358		

TEMPERATURE, DEGREES CENTIGRADE	SPECIFIC HEAT
0 and 23.5	0.1653
0 and 99.22	0.1935
0 and 223.6	0.2385

The calorific value of charcoal is high in comparison with wood, as will be observed from Klason's[4] data. The composition

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[1] W. LUZI, *Ber.*, **25** (1892), 1383.

[2] L. F. HAWLEY, *J. Ind. Eng. Chem.*, **13** (1921), 301; U. S. P. 1369428 (1921).

[3] L. KUNZ, *Ann. Physik*, **14** (1904), 323; H. F. WEBER, *Pogg. Ann.*, **154**, (1875), 560.

[4] P. KLASON *et al.*, *Z. angew. Chem.*, **23** (1910), 1252, 1256.

CALORIFIC VALUE OF WOOD AND CHARCOAL

Species	Wood calorific value, calories	Charcoal			
		Composition, per cent			Calorific value, calories
		C	H	O	
Pine	5,070	82.5	4.0	13.5	7,685
Spruce	4,910	82.5	4.1	13.4	7,695
Birch	4,910	82.2	3.8	14.0	7,680
Beech	4,790	82.1	4.1	13.8	7,555

of the charcoal agrees closest with the formula $C_{16}H_{10}O_2$. Owing to the avidity with which charcoal takes up moisture and oxygen, analyses must not be accepted as representing the charcoal as it left the retort. According to Nikitin,[1] the heat of combustion of 1 gram of charcoal may be closely calculated from the formula

$$\text{Heat of combustion} = 80.51\ C + 273.4\ H,$$

in which C and H represent the percentages of carbon and hydrogen in the dry charcoal. When tested with Klason's data, the formula is not reliable.

Charcoal that has been subjected to a current of 2200 amperes and 60 volts for 10 minutes retains its structural form but gives graphitic acid on oxidation.[2] Judging from conductivity measurements,[3] graphitization begins at about 1200°.

PREPARATION TEMPERATURE, DEGREES CENTIGRADE	CONDUCTIVITY, MILLIAMPERES
700	0.004
1150	67.00
1200	210.00
1400	340.00

To obtain a graphite similar to the natural product, a temperature of about 3000° is usually employed.[4]

Wood charcoal is not affected by concentrated sulphuric acid in the cold.[5] Hot concentrated sulphuric and nitric acids produce benzene polycarboxylic acids by oxidation. Boiling concentrated sodium hydroxide dissolves charcoal with the evolution of hydrogen but not of carbon monoxide.[1]

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[1] N. I. NIKITIN, C. A., **11** (1917), 746.

[2] H. MOISSAN, *Ann. chim. phys.*, [7] **8** (1896), 323.

[3] H. HERBST, *Biochem. Z.*, **115** (1921), 213.

[4] C. ARSEM, *Trans. Am. Electrochem. Soc.*, **20** (1911), 110.

[5] M. BERTHELOT, *Ann. chim. phys.*, [7] **14** (1898), 206.

Freshly prepared charcoal is highly combustible. It appears to absorb oxygen for 36 hours after carbonization. If powdered and stored before the expiration of this time, it will take fire spontaneously when exposed to the air.[2] Jacobs[3] has prepared from soda pulp "black liquor," a form of carbon that is highly reactive towards oxygen. It unites with atmospheric oxygen when heated to 150°; with some samples, at as low as 80°. The continuous absorption of oxygen by charcoal at ordinary temperatures over long periods of time results essentially in the formation of a solid oxide of carbon.[4] Heating produces decomposition with the formation of carbon monoxide and carbon dioxide.

It had long been known that wood treated with various chemicals, such as acids and acid salts, charred, and washed gave a charcoal with greatly increased adsorptive powers.[5] It is stated[6] that the activated charcoal used in German gas masks was prepared by treating wood with a small amount of hydrochloric acid and zinc chloride, charring, and washing.

Opinions differ as to the reasons for the high activity of a charcoal. The amount and nature of the ash greatly influences the development of surface activity. According to Herbst,[7] high adsorptive power is a specific property of pure, free, chemically unsaturated carbon. Wood charcoal shows increased adsorption with increase in carbon content and decrease in hydrogen. The adsorptive power for gases increases on heating up to 1150° but decreases above 1200°.

According to Chaney,[8] all "primary" amorphous carbons consist of a stabilized complex of hydrocarbons adsorbed on a base of active carbon. Small quantities of a hydrocarbon, b.p. 360°, were isolated from cedar-wood charcoal that had been heated to 850°. To obtain a highly active carbon, it is necessary to remove the hydrocarbons; though the removal can be accomplished by high temperatures, the carbon is rendered inactive. It is possible to break down the hydrocarbons below the point at which inactive carbon is formed by means of air, steam, carbon dioxide, salts, and other chemical reagents.

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[1] F. Haber and L. Bruner, *Z. Elektrochem.*, **10** (1894), 697.

[2] A. Hargreaves, *J. Chem. Soc.*, **12** (1874), 420.

[3] C. B. Jacobs, *Chem. Age*, **31** (1923), 475; U. S. P. 1462752 (1923).

[4] H. H. Lowry and G. A. Hulett, *J. Am. Chem. Soc.*, **42** (1920), 1393.

[5] H. L. Melsens, *Compt. rend.*, **79** (1874), 375; R. Ostrejko, E. P. 14224 (1900).

[6] F. H. Carr, *J. Soc. Chem. Ind.*, **38** (1919), 468R.

[7] H. Herbst, *Biochem. Z.*, **115** (1921), 205.

[8] N. K. Chaney, *Trans. Am. Electrochem. Soc.*, **36** (1919), 91.

The nature of the medium in which the charcoal has been heated greatly affects the activity, since a small amount of the gas is retained as a complex.[1] In the following table the activity was measured by the amount of phenol taken up from a 1 per cent solution at 25° by 100 grams of alder-wood charcoal.

	Medium								
	N	CO	Cl	Steam	CO_2	NH_3	S	SO_2	Air + N
Temperature, degrees Centigrade	1200	1000	1000	850	850	900	1000	675	300
Adsorption	1.5	1.5	0	25	25	35	0	30	15

It is necessary to treat the carbon in different ways in order to obtain maximum adsorption of any particular compound.

Constitution and Composition of Charcoal.—It has been concluded from X-ray examinations that amorphous carbon is identical with graphite, differing from it only in its greater degree of subdivision.[2] There is at least one marked chemical difference. On oxidation, graphite gives graphitic acid and charcoal mellitic acid, mainly.

Mellitic acid[3] is a characteristic product of the oxidation of most wood charcoals. Verneuil,[4] by means of concentrated sulphuric acid, obtained mellitic, benzene pentacarboxylic, and benzene tetracarboxylic acids. On oxidation with fuming nitric acid,[5] charcoal gave 25 per cent of ammonium mellitate. No difference was noted in the yield, if the charcoal contained 2.0 or 0.2 per cent of hydrogen.

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[1] O. Ruff *et al.*, *Kolloid-Z.*, **32** (1923), 225.

[2] P. Debye and P. Scherrer, *Physik. Z.*, **18** (1917), 291.

[3] F. Schulze, *Ber.*, **4** (1871), 801.

[4] A. Verneuil, *Compt. rend.*, **118** (1894), 195; **132** (1901), 1340; *cf.* E. Philippi and R. Thelen, *Ann.*, **428** (1922), 296.

[5] M. A. Dickson and T. H. Easterfield, *Proc. Chem. Soc.*, **14** (1898), 163; *cf.* E. P. 24662 (1907); E. Philippi and G. Rie, *Ann.*, **428** (1922), 287

Since charcoal yields mellitic acid, it has been assumed that the carbon exists as six-membered rings, each carbon atom being attached to carbon atoms without the ring. The barium salts of the benzene carboxylic acids, obtained by oxidizing charcoal with nitric acid, gave on distillation benzene, napthalene, and fluorene. It was concluded from the presence of fluorene that charcoal also contains bodies with a five-membered ring.[1] Various structures[2] have accordingly been assigned to the carbon molecule. Aschan[3] considers charcoal to be a hydrocarbon of high molecular weight, having the formula $(C_{130}H_{10})_x$ or $(C_{132}H_{10}O)_x$. He proposes a honeycomb ring structure and suggests that the dark color of charcoal may be due to quinoidal linkages.

It is reasonably certain that ordinary charcoal contains, in addition to free carbon, quantities of hydrocarbons as a residue from incomplete distillation. If charcoal is subjected to a white heat, oxidizing agents attack it very slowly and the yield of mellitic acid is almost nothing.[4] Meyer[5] concludes that the formation of mellitic acid has no bearing on the constitution of the carbon molecule. The yield of mellitic acid from different wood charcoals varied from 0 to 40 per cent, the highest yields being obtained from coniferous charcoal.

Composition of Distillates.—A large number of compounds have been identified in the pyroligneous acid and tar. These compounds are listed on pages 465–467. Most of them occur in very small amounts. For example, crude methyl alcohol does not contain more than 0.2 per cent of allyl alcohol, as was determined by refining 50,000 pounds of the crude alcohol.[6] The fraction high in allyl alcohol, obtained in the refining process, is one of the few cheap sources for this alcohol.

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[1] O. Dimroth and B. Kerkovius, *Ann.*, **399** (1913), 120.

[2] J. Dewar, *Chem. News*, **97** (1908), 16; H. S. Redgrove, *Ibid.*, 37; J. C. Thomlinson, *Ibid.*, 37; H. E. Armstrong, *J. Soc. Chem. Ind.*, **24** (1905), 478.

[3] O. Aschan, *Chem. Ztg.*, **33** (1909), 561–562.

[4] A. Verneuil, *Compt. rend.*, **132** (1901), 1340.

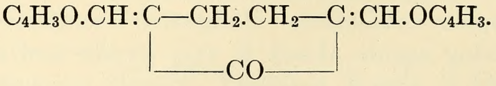
[5] H. Meyer, *Monatsh.*, **35** (1914), 163.

[6] M. Grodzki and G. Kraemer, *Ber.*, **7** (1874), 1494.

The composition of pyroligneous acid and wood tar was long hedged about with uncertainty.[1] Many of the supposedly definite compounds were mixtures; thus, dumasin is a mixture of methyl-α-butenylketone and cyclopentanone.[2] Hermilian[3] reported the presence of ethyl alcohol in crude methyl alcohol, but it could not be detected in the fraction, b.p. 70 to 100°, from 24,000 kilograms of raw material.[4] Though frequently reported, Fraps[5] could not find mesityl oxide or other condensation products of acetone in the oil from hardwood tar. He reports minute quantities of nitriles.

The oils from hardwood tars contain small quantities of sulphur compounds, possibly thiophenols.[6] Pastrovitch[7] isolated a phenol (coerulignol), $C_{10}H_{14}O_2$, that is possibly propyl-pyrogallol.

Pyroxanthine (difurfural-ketopentamethylene) does not exist in the original pyroligneous acid. It is produced by condensation[8] of furfural with adipic ketone when the pyroligneous acid is treated with lime.



$$C_4H_3O.CH{:}\underbrace{C{-}CH_2.CH_2{-}C}_{CO}{:}CH.OC_4H_3.$$

The wine-red color produced on neutralizing pyroligneous acid with lime is obtained only when the lime contains traces of ferric salts. The indicator probably consists of the ethers of pyrogallol and its homologs.[9]

Oxidation of the higher phenol ethers gives dimethoxyquinone and coerulignone.[10] Coerulignone (cedriret) has the composition $C_{16}H_{16}O_6$ and is apparently a tetramethoxy-*p*, *p*′-

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[1] An interesting history of wood creosote is given by C. S. Schorlemmer, *J. Soc. Chem. Ind.*, **4** (1885), 152–157.

[2] H. Pringsheim and J. Leibowitz, *Ber.*, **56** (1923), 2034.

[3] V. Hermilian, *Ber.*, **8** (1875), 661, 768.

[4] Verein f. Chemische Ind. zu Frankfort, *Chem. Ztg.*, **20** (1896), 1015.

[5] G. S. Fraps, *Am. Chem. J.*, **25** (1901), 28.

[6] A. Béhal and E. Choay, *Compt. rend.*, **118** (1894), 1339.

[7] P. Pastrovitch, *Monatsh.*, **4** (1883), 188.

[8] D. Vorländer and K. Hobohm, *Ber.*, **29** (1896), 1838.

[9] J. M. Johlin, *J. Ind. Eng. Chem.*, **7** (1915), 596.

[10] C. Liebermann, *Ber.*, **5** (1872), 746; **6** (1873), 381; **8** (1875), 69; *Ann.*, **169** (1873), 221; A. W. Hofmann, *Ber.*, **7** (1874), 78.

diphenyl quinone, though there are several possible structures.[1] Dimethoxy-quinone has been prepared by the oxidation of propyl-pyrogallol-dimethyl-ether[2] and pyrogallol-trimethyl-ether.[3]

Hardwood tars are usually richer in phenols, especially guaiacol, than the softwood tars; however, the tar from the distillation of redwood[4] is reported to possess an usually high phenol content.

Medicinal wood creosote is usually prepared from beech, birch, and maple. It should distil mainly between 200 and 210°, though the composition will vary with the species. Béhal and Choay[5] found that beech-wood creosote contained more guaiacol and less monophenols than oak-wood creosote. The phenol fraction of a beech-wood creosote, b.p. 200 to 210°, had the following composition:

	Per Cent		Per Cent
Phenol	5.20	1, 3, 4-Xylenol	2.00
o-Cresol	10.40	1, 3, 5-Xylenol	1.00
m- and *p*-Cresols	11.60	Various phenols	6.20
o-Ethylphenol	3.06	Creosol and homologs	35.00
Guaiacol	25.00		

The phenol fraction, b.p. 190 to 230°, from a pine tar examined by Renard[6] contained:

	Per Cent
Monophenols	40.0
Guaiacol	20.3
Creosol and homologs	37.5

Wood creosote is prepared by extracting the phenols from the heavy tar oils, b.p. 190 to 240°, with alkali. The best quality of creosote is obtained by extracting with an amount of 5 per cent sodium hydroxide such that only about two-fifths of the phenols present are dissolved.[7]

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[1] C. Liebermann and J. Flatau, *Ber.*, **30** (1897), 234; A. W. Hofmann, *Ibid.*, **11** (1878), 801.

[2] A. W. Hofmann, *Ber.*, **11** (1878), 329.

[3] W. Will, *Ber.*, **21** (1888), 608.

[4] W. H. Hund, U. S. P. 1365407 (1921).

[5] A. Béhal and E. Choay, *Compt. rend.*, **119** (1894), 166; *cf.* L. F. Kebler, *Am. J. Pharm.*, **71** (1899), 409–413.

[6] A. Renard, *Compt. rend.*, **119** (1894), 1276.

[7] L. F. Hawley, U. S. P. 1199271 (1916).

The antiseptic properties of wood smoke are attributed to aliphatic aldehydes, especially formaldehyde. The smoke from 100 grams of wood contained 0.5 gram of formaldehyde.[1]

Spruce tar decomposed at a red heat gave benzene, toluene, napthalene, and anthracene.[2]

Wood tar contains small amounts of the higher fatty acids. Bornstein[3] obtained 4 grams of palmitic acid and 2 grams of oleic acid from 1 kilogram of pine tar. According to Marcusson and Picard,[4] wood tar and pitch, particularly from hardwoods, are high in oxyacids. The pitch may also contain condensation products[5] of aldehydes, ketones, and phenols.

Composition of Wood Tar and Pitch

Product	Unsaponifiable, per cent	Anhydrides of oxyacids, per cent	Oxyacids		Resin acids, per cent	Fatty acids, per cent	Phenols, per cent
			Ether insoluble, per cent	Ether soluble, per cent			
Beech tar	18	9.5	33.3	19	7.7	3.2	9.3
Beech pitch	6	77			0	1.5	1.5
Pine tar	53.5	0	14		17	6	9.5
Pine pitch	19.7	31.8			35.2	2.8	8.0

The distillate from resinous woods contains resin acids and terpenes, and their decomposition products. Resin acids and terpenes are secondary constituents of wood. The terpenes will vary with the particular species of wood. Adams[6] found the oils from the wood of *Pinus monophylla*, *Pinus jeffreyi*, and *Pinus ponderosa* to contain practically the same constituents as Schorger had identified in the oleoresins of the same species; however, the volatile oils from the wood and oleoresin are seldom identical. The oil from the oleoresin usually consists entirely of hydrocarbons. In the course of time the terpenes in the heartwood undergo rearrangement and hydration with the formation of volatile oils of entirely different properties, such as the "wood turpentine" and "pine oil" distilled from the wood of the southern pines. Teeple[1] found that pine oil consisted mainly of α-terpineol. A thorough investigation of this oil by Schimmel and Company[2] revealed the following constituents:

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[1] G. Pasqualis, *Chem. Zentr.*, **68,** II (1897), 1012.

[2] A. Atterberg, *Ber.*, **11** (1878), 1222.

[3] E. Bornstein, *J. Gasbel.*, **63** (1920), 90; *cf.* G. P. 314358 (1917).

[4] J. Marcusson and M. Picard, *Z. angew. Chem.*, **34** (1921), 201–204; *Chem. Umschau Fette, Oele, Wachse u. Harze*, **28** (1921), 257–258.

[5] R. P. Duchemin, *Bull. Soc. Chim.*, **7** (1910), 473.

[6] M. Adams, *J. Ind. Eng. Chem.*, **7** (1914), 957–960.

α-Pinene
β-Pinene
Camphene
l-Limonene
Dipentene
γ-Terpinene
Cineol
Camphor
Methyl-chavicol
Borneol
α-Terpineol
Fenchyl alcohol
Isofenchyl alcohol

A list of the numerous decomposition products of rosin, and the terpenes, obtained on distilling resinous wood from various species, does not fall within the province of this work.

Source of Products.—It is useless to hazard an opinion on the groupings within the cellulose and lignin molecules that give rise to the products of wood distillation. The former confidence in pyrolytic decomposition as a method for determining constitution is now deservedly wanting; however, Klason[3] has advanced a formula for lignin by which he explains the formation of phenols and phenol ethers, 2-methyl-furan, and allyl and methyl alcohol.

The source of some products can be definitely assigned to cellulose or lignin by the process of elimination. Cellulose gives only small amounts of phenols, so that the large number of phenols and phenol ethers obtained from wood have their origin in the lignin. Lignin is profoundly modified by all available methods for its isolation, so that distillation of the modified product does not give reliable information as to what is obtainable from the original.

Methyl alcohol is derived solely from methoxyl groups in the lignin, cellulose yielding no methyl alcohol on distillation. Allyl alcohol, also, is derived from the lignin.

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[1] J. E. Teeple, *J. Am. Chem. Soc.*, **30** (1908), 412.

[2] Schimmel & Co. *Report* for April (1910), 104–109.

[3] P. Klason, *Ber.*, **56** (1923), 300.

Acetic acid is formed from acetyl groups in the lignin and by decomposition of the cellulose. The presence of formyl groups in lignin has not been satisfactorily established. Formic acid is probably formed mainly by decomposition of the carbohydrates, hydrolysis first taking place in the presence of organic acids, at the prevailing high temperature. The hexose sugars would decompose partially into formic and lævulinic acids.

$$C_6H_{12}O_6 \rightarrow \underset{\text{Lævulinic acid}}{CH_3.CO.CH_2.COOH} + \underset{\text{Formic acid}}{H.COOH} + H_2O.$$

Lævulinic acid on distillation gives the lactone of angelic acid, and on reduction, valeric acid.

Aschan[1] has suggested that some of the aliphatic acids are formed from the hexoses as follows:

$$C_6H_{12}O_6 \rightarrow \underset{\text{Acetic acid}}{3CH_3.COOH}.$$

$$C_6H_{12}O_6 \rightarrow \underset{\text{Propionic acid}}{CH_3.CH_2.COOH} + \underset{\text{Acetic acid}}{CH_3.COOH} + \underset{\text{Formic acid}}{H.COOH}.$$

$$C_6H_{12}O_6 \rightarrow \underset{\text{Butyric acid}}{CH_3.CH_2.CH_2.COOH} + 2H.COOH.$$

Glucose on destructive distillation[2] gives formic and acetic acids, formaldehyde, acetone, methylfuran, furan, furfural, carbon dioxide, carbon monoxide, and methane.

Furfural is formed mainly from pentosans. Furan and its homologs occur in the distillate from cellulose. It is not known if lignin free from carbohydrates will give furan, though a furan structure has been suggested for lignin.

The ketones are probably formed by a secondary decomposition of the fatty acids. The small amount of protein in wood furnishes the ammonia and pyridine.

Wood on distillation yields larger quantities of methane than does cellulose. This must be due to the formation of methane from methoxyl groups.[3]

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[1] O. Aschan, *Z. angew. Chem.*, **26** (1913), 711.

[2] E. von Lippmann, "Die Chemie der Zuckerarten," I (1904), 301.

[3] L. F. Hawley and S. S. Aiyar, *J. Ind. Eng. Chem.*, **14** (1922), 1056.

Constituents of Hardwood Pyroligneous Acid[1]

Acids and Lactones

Formic	1, 6, 9	Caproic	9
Acetic	1	Angelic	6
Propionic	5, 6, 9	α- and β-Crotonic	6
n-Butyric	5, 6, 9	Dihydroxyoctoic	32
n-Valeric	5, 6, 9	$C_7H_{13}(OH)_2.COOH$	
Valerolactone	8		

Alcohols

Methyl	1, 2	Methyl-allyl	33
Allyl	3, 4	$CH_3.CH(OH).CH{:}CH_2$	

Esters

Methyl acetate	2, 10	Methyl formate	10

Aldehydes and Derivatives

Formaldehyde	7, 48	Isovaleraldehyde	32
Acetaldehyde	4, 7, 10	Furfural	1, 11
Dimethyl-acetal	2	2-Methylfurfural	12
Trimethyl-acetaldehyde	32	Pyroxanthine	53, 54, 55

Ketones

Acetone	1, 1*a*, 2, 10	Adipic ketone (cyclopentanone)	23, 24, 32
Diethyl ketone	33	Methyl-α-butenyl ketone	32
Diacetyl	40	Methyl-cyclopentenolone	28
Methylpropyl ketone	22	2-Keto-3-hexene	32
Methylethyl ketone	22, 31, 32	$CH_3.CO.CH{:}CH.CH_2.CH_3$	
Succinyl ketone	23		

Bases

Ammonia	1	Pyridine	23

Hydrocarbons

Toluene	19, 22	Cumene	19
Xylene	19, 22		

Furans

α, α-Dimethyl-tetrahydrofuran	33
α-Methyl-ά-ethyl-ά, β́-dihydrofuran	33

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[1] Figures are to references at end of chapter.

CONSTITUENTS OF HARDWOOD TAR

Acids and Lactones

Lignoceric	29, 52	Dokozanic $C_{21}H_{41}O_2$ or $C_{22}H_{44}O_2$	36

Alcohols

Isoamyl	20	Isobutyl	21

Esters

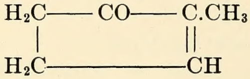
Methyl acetate	13	Methyl-*n*-butyrate	13
Methyl propionate	13	Methyl-*n*-valerate	13

Aldehydes

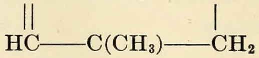
Valeraldehyde	13	Propionaldehyde	16

Ketones

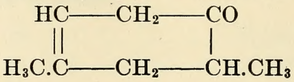
Methylethyl ketone	13
Methyl-*n*-propyl ketone	13
Methyl-*n*-butyl ketone	13
Diethyl ketone (?)	13
Adipic ketone	13
Pimelic ketone (cyclohexanone)	21
Methyl-cyclopentenone	20, 25



Methyl-cyclohexenone	26



Dimethyl-cyclohexenone	27



Bases

Pyridine	20	Dimethyl-pyridine	20, 21

Furans

α-Methyl-furan	13, 14	Trimethyl-furan	13
Dimethyl-furan	13, 16	1, 2-Acetyl-furan	25

Phenols

Phenol	17, 18, 30, 37	Catechol	49
o-Cresol	37	Guaiacol	17, 18, 30, 38
m-Cresol	37	1, 3, 4-Ethyl-guaiacol	37
p-Cresol	17, 18, 30, 37	Methyl-catechol-dimethyl-ether	30*a*
o-Ethyl-phenol	37	Pyrogallol-dimethyl-ether	30, 41, 44
1, 3, 4-Xylenol	17, 30, 37, 39	Methyl-pyrogallol-dimethyl-ether	30, 41, 45
1, 3, 5-Xylenol	37	Propyl-pyrogallol-dimethyl-ether	30, 41, 44, 46
Creosol	17, 30, 38		

Constituents of Softwood Pyroligneous Acid and Tar

Acids

Formic	50	Caprylic	50
Acetic	50	Oleic	47
Propionic	50	Palmitic	47
n-Butyric	50, 51	Arachidic	47
Valeric	42, 50	Abietic	47
α-Methyl-valeric	50	Pimaric	42
Caproic	42, 50		
Œnanthylic	42, 50		

Alcohols

Methyl	51	Allyl	51

Esters

Methyl-isobutyrate	34

Aldehydes

Acetaldehyde	35	Furfural	34
Propionaldehyde	35		

Ketones

Acetone	35, 51	Diacetyl	34

Furans

Furan	34	Dimethyl-furan	34
α-Methyl-furan	15, 34		

Hydrocarbons

Benzene	34	*m*-Xylene	34
Toluene	34	Retene	43, 50, 51

Phenols

Phenol	50	Guaiacol	42, 50
Cresol	50	1, 3, 4-*n*-Propyl-guaiacol	42, 50
Creosol	42, 50	1, 3, 4-Ethyl-guaiacol	42, 50

References

1. C. Völckel, *Ann.*, **86** (1853), 66–113.
1*a*. C. Völckel, *Ann.*, **80** (1851), 310.
2. W. Dancer, *Ann.*, **132** (1864), 240–243.
3. B. Aronheim, *Ber.*, **7** (1874), 1381–1382.
4. M. Grodzki and G. Kraemer, *Ber.*, **7** (1874), 1492–1497.
5. T. Anderson, *Chem. News*, **14** (1866), 257.
6. G. Kraemer and M. Grodzki, *Ber.*, **11** (1878), 1356–1362.

7. R. P. Duchemin, *Bull. soc. chim.*, [4] **7** (1910), 477.
8. M. Grodzki, *Ber.*, **17** (1884), 1369.
9. Barré, *Compt. rend.*, **68** (1869), 1222–1224.
10. C. F. Mabery, *Am. Chem. J.*, 5 (1883), 256–263.
11. H. B. Hill, *Ber.*, **10** (1877), 936–993.
12. H. B. Hill, *Ber.*, **22** (1889), 607; H. B. Hill and W. L. Jennings, *Am. Chem. J.*, **15** (1893), 159.
13. G. S. Fraps, *Am. Chem. J.*, **25** (1901), 26–53.
14. C. Harries, *Ber.*, **31** (1898), 37–47.
15. A. Atterberg, *Ber.*, **13** (1880), 879–883.
16. E. Fischer and W. J. Laycock, *Ber.*, **22** (1889), 105.
17. S. Marasse, *Ann.*, **152** (1869), 59–87; *Ber.*, **1** (1868), 99–100; *Ibid.*, **2** (1869), 71–73.
18. E. von Gorup-Besanez, *Ann.*, **86** (1853), 223–258; *Ibid.*, **143** (1867), 129–174.
19. A. Cahours, *Ann.*, **76** (1850), 286–287.
20. E. Looft, *Ann.*, **275** (1893), 366–382.
21. E. Looft, *Ber.*, **27** (1894), 1542–1546.
22. Vladesco, *Bull. soc. chim.*, **3** (1890), 510–514.
23. W. Hentzschel, *Ann.*, **275** (1893), 318–322.
24. D. Vorländer and K. Hobohm, *Ber.*, **29** (1896), 1836; H. Metzner and D. Vorländer, *Ibid.*, **31** (1898), 1885–1886.
25. L. Bouveault, *Compt. rend.*, **125** (1897), 1184–1186.
26. A. Béhal, *Compt. rend.*, **126** (1898), 46–49; *cf. Ibid.*, **125** (1897), 1036–1038.
27. A. Béhal, *Compt. rend.*, **132** (1901), 342–345.
28. J. Meyerfeld, *Chem. Ztg.*, **36** (1912), 549–552.
29. C. Hell, *Ber.*, **13** (1880), 1709–1713; *Ibid.*, 1713–1751.
30. F. Tiemann and P. Koppe, *Ber.*, **14** (1881), 2005–2014.
30*a*. F. Tiemann and B. Mendelsohn, *Ber.*, **8** (1875), 1136–1139.
31. G. Kraemer and M. Grodzki, *Ber.*, **9** (1876), 1920–1927.
32. H. Pringsheim and J. Leibowitz, *Ber.*, **56** (1923), 2034–2041.
33. H. Pringsheim and A. Gorgas, *Ber.*, **57** (1924), 1561–1566.
34. O. Aschan, *Z. angew. Chem.*, **20** (1907), 1811–1816.
35. O. Aschan, *Z. angew. Chem.*, **26** (1913), 709–713.
36. I. K. Traubenberg, *J. Soc. Chem. Ind.*, **42** (1923), 303A.
37. A. Béhal and E. Choay, *Compt. rend.*, **118** (1894), 1339–1342; **119** (1894), 166–169.
38. H. Hlasiwetz, *Ann.*, **106** (1858), 339.
39. M. Pfränger, *Arch. Pharm.*, **228** (1890), 713–719.
40. J. M. Johlin, *J. Am. Chem. Soc.*, **37** (1915), 892.
41. E. J. Pieper, S. F. Acree, and C. J. Humphrey, *J. Ind. Eng. Chem.*, **9** (1917), 462–465.
42. M. Nencki and N. Sieber, *Arch. Exp. Path. Pharm.*, **33** (1894), 17.
43. A. Wahlforss, *Chem. Zentr.*, **40** (1869), 479.
44. A. W. Hofmann, *Ber.*, **11** (1878), 329–338; *cf. Ibid.*, **8** (1875), 66.
45. A. W. Hofmann, *Ber.*, **12** (1879), 1371.

46. G. Niederist, *Monatsh.*, **4** (1883), 487–493; *cf.* P. Pastrovitch, *Ibid.*, 182–187.
47. E. Bornstein, *J. Gasbel.*, **63** (1920), 90.
48. P. Klason, *J. prakt. Chem.*, **90** (1924), 413.
49. M. Pettenkofer, *J. prakt. Chem.*, **62** (1854), 508; M. Buchner, *Ann.*, **96** (1885), 188–193.
50. K. Ström, *Arch. Pharm.*, **237** (1899), 525–543.
51. J. A. Mjoen, *Z. angew. Chem.*, **15** (1902), 97–111.
52. M. X. Sullivan, *J. Ind. Eng. Chem.*, **8** (1916), 1027.
53. W. Gregory, *Ann.*, **21** (1837), 143.
54. H. B. Hill, *Ber.*, **10** (1877), 936; **11** (1878), 456.
55. D. Vorländer and K. Hobohm, *Ber.*, **29** (1896), 1838.

CHAPTER XIV

THE FERMENTATION OF CELLULOSE AND WOOD BY BACTERIA AND FILAMENTOUS FUNGI

The fungi have always played an important rôle in the life of man, but it is only within recent years that their economic possibilities have received the careful attention that they deserve. The utilization of wood waste of small dimension is still largely an unsolved problem. Nature has provided for the disposal of wood through the fungi. Controlled "decay" by organisms yielding products of value would appear to be a logical procedure, even though the trend of science has been for synthesis *in vitro* and the elimination of biological processes.

Fermentation of Cellulose by Bacteria.—The bacteria able to decompose cellulose may be divided into two main groups, aerobic and anaerobic. In the former, fermentation takes place in the presence of free oxygen, and in the latter, in its absence. Pringsheim[1] gives the following classification:

Group	Fermentation Products
1. Methane bacteria......	CH_4, CO_2, and lower fatty acids to butyric acid.
2. Hydrogen bacteria.....	H_2, CO_2, and lower fatty acids to butyric acid.
3. Thermophilic bacteria..	CH_4, H_2, CO_2, formic and acetic acids.
4. Denitrifying bacteria...	N_2 and CO_2.

In 1850, Mitscherlich[2] observed that the cell walls enclosing the starch granules in the potato were destroyed by microorganisms. He attributed the fermentation of the cellulose to vibrios which were present in large numbers. Popoff[3] made the first important contribution to the subject by showing the relation between the formation of methane in nature and the fermentation of cellulose. Filter paper fermented by slime from the sewers of Strassburg, 38 to 40° being the optimum temperature, gave a gas containing carbon dioxide, methane, hydrogen, and nitrogen. The gas collected after 4 weeks contained much less hydrogen than that collected at the end of 2 weeks. It was concluded that hydrogen formation was not due to the cellulose fermentation proper.

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[1] H. Pringsheim, *Z. physiol. Chem.*, **78** (1912), 270.

[2] Mitscherlich, *Monatsber. k. Acad. Wiss. Berlin* (1850), 104; cited by F. Hoppe-Seyler, *Z. physiol. Chem.*, **10** (1886), 403.

[3] L. Popoff, *Arch. Physiol.*, **10** (1875), 113–146.

The experiments of Hoppe-Seyler[1] supported the belief that the decomposition of cellulose was a methane fermentation. A flask containing a substrate of filter paper inoculated with sewage was kept for four years. The gas evolved contained carbon dioxide and methane but no hydrogen. Hoppe-Seyler concluded that the cellulose was first hydrolyzed to glucose, then the latter quantitatively converted into carbon dioxide and methane.

$$C_6H_{12}O_6 = 3CO_2 + 3CH_4.$$

The living organism could not be distinguished from the *Bacillus amylobacter* described by van Tieghem[2] as fermenting certain natural celluloses.

In 1895, Omelianski[3] contributed the first of a long series of papers on the fermentation of cellulose. A bacillus capable of fermenting filter paper was isolated from the mud of the river Niva. A similar organism, *Bacillus fermentationis cellulosæ*,[4] obtained from soil rich in vegetable débris,[5] gave under anaerobic conditions about 70 per cent of fatty acids, acetic, butyric, and valeric, and 30 per cent of hydrogen and methane.

The cultures obtained from soil or horse manure were not pure,[6] since according to experimental conditions a hydrogen or methane fermentation resulted. If the culture was first heated to 75° for about 15 minutes, and then held at 35°, the hydrogen fermentation predominated, while without the preliminary heating the methane fermentation was much the stronger. Morphologically, the two organisms were very similar.

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[1] F. Hoppe-Seyler, *Z. physiol. Chem.*, **10** (1886), 201–217, 401–440; *Ber.*, **16** (1883), 122–123.

[2] P. E. L. van Tieghem, *Bull. Soc. Botan. France*, **24** (1877), 128–135; *Compt. rend.*, **88** (1879), 205–210; *Ibid.*, **89** (1879), 5–8.

[3] W. Omelianski, *Compt. rend.*, **121** (1895), 363–365.

[4] W. Omelianski, *Arch. Soc. Biolog. St. Petersb.*, **7** (1900), 411–434.

[5] W. Omelianski, *Compt. rend.*, **125** (1877), 970–973, 1131–1133.

[6] W. Omelianski, *Chem. Ztg.*, **26** (1902), 133; *Centr. Bakt., Parasitenk.*, II Abt., **11** (1904), 369–377; *cf. Ibid.*, II Abt., **8** (1902), 193–201, 225–231, 257–263, 289–294, 321–326, 353–361, 385–391; II Abt., **12** (1904), 33–43; II Abt., **15** (1906), 673–687.

Kellerman and McBeth[1] isolated two species of cellulose-fermenting bacteria, and five species of contaminating bacteria, from Omelianski's hydrogen culture, and one cellulose-destroying and two contaminating species, from the methane culture. Contrary to the results of Omelianski, the three cellulose-fermenting organisms isolated attacked the cellulose most rapidly under aerobic conditions, and did so without the production of gas.

Five species of bacteria that ferment cellulose are described by McBeth and Scales.[2] The fermentation products were mainly the lower fatty acids. Gaseous products resulted from secondary fermentation by contaminating organisms, and not from the cellulose ferments. Not only the purity of the cultures of Kellerman and McBeth, but their ability to dissolve cellulose has been questioned.[3]

It has also been questioned whether a pure cellulose-fermenting organism has ever been isolated. There is evidence to the effect that cellulose is destroyed only by the symbiotic action of several organisms. Van Senus[4] found that cellulose was destroyed by the joint action of *B. amylobacter* and an organism isolated from the intestines of a rabbit, neither being effective alone. He concluded that methane was not formed directly. The cellulose was decomposed into hydrogen, carbon dioxide, and acetic acid, the hydrogen reducing the acetic acid to methane.

The anaerobic decomposition of cellulose proceeds differently in the presence and absence of nitrates.[5] In their presence, the cellulose is decomposed by denitrifying bacteria with the formation of nitrogen, carbon dioxide, and water. Among aerobic, non-sporulating bacteria, *Bacterium ferruginens* is most important and active, in symbiosis with a yellow micrococcus itself inactive.

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[1] K. F. Kellerman and I. G. McBeth, *Centr. Bakt., Parasitenk.*, II Abt., **34** (1912), 63–64, 485–494; I. G. McBeth, *Soil Science*, **1** (1916), 437–487; *cf.* F. Löhnis and G. Lochhead, *Centr. Bakt., Parasitenk.*, II Abt., **37** (1913), 490–492.

[2] I. G. McBeth and F. M. Scales, "The Destruction of Cellulose by Bacteria and Filamentous Fungi," *Bull.* **266,** *U. S. Dept. Agr.* (1913).

[3] H. Pringsheim and S. Lichtenstein, *Centr. Bakt., Parasitenk.*, II Abt., **60** (1923), 309–311.

[4] A. H. C. van Senus, *Jahresb. Fortschritte Lehre Gärungs-Organismen,* **1** (1890), 136–139.

[5] C. van Iterson, Jun., *Centr. Bakt., Parasitenk.*, II Abt., **11** (1904), 689–698.

Groenwege[1] studied the fermentation of cellulose, in a medium containing nitrates, using organisms from soil and septic tank liquid. There was denitrification and destruction of the cellulose, but as a result of the action of two classes of organisms. The α-, β-, and γ-forms of *Bacillus cellaresolvens* attacked the cellulose, producing acetic, butyric, and lactic acids. These degradation products served as food for the denitrifying organisms, *B. opalescens* and *B. viscosus*, themselves incapable of attacking cellulose.

Löhnis and Lochhead[2] consider the conclusion inevitable that the most active cellulose bacteria must have the symbiotic assistance of other microorganisms in the destruction of cellulose.

A large number of organisms, whose individuality and power to ferment normal cellulose may be questioned, have been described. There may be mentioned: *Bacillus cellulosæ desaggregans* from the intestines of fowls;[3] *Micrococcus cytophagus* and *M. melanocyclus* from decayed radishes.[4]

An aerobic organism, (*Spirochæta cytophaga*) isolated from Rothhamsted soil by Hutchinson and Clayton,[5] decomposes cellulose readily with the formation of a yellow pigment, fatty acids, and a mucilage resembling pectin. Its optimum temperature is 30°. Carbohydrates other than cellulose do not support growth. Advantage has been taken of this, and related organisms, to produce an artificial manure by the fermentation of straw to which nitrogenous substances have been added.[6] The fermentation, requiring about 3 months, is being commercialized as the "Adco" process.

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[1] J. Groenwege, *J. Soc. Chem. Ind.*, **40** (1921), 76A.

[2] F. Löhnis and G. Lochhead, *Centr. Bakt.*, *Parasitenk.*, II Abt, **58** (1923), 434.

[3] A. Diastaso, *Compt. rend. soc. biol.*, **70** (1912), 995.

[4] A. Peche, G. P. 292482 (1913).

[5] H. B. Hutchinson and J. Clayton, *J. Agr. Sci.*, **9** (1919), 143–173.

[6] H. B. Hutchinson and E. H. Richards, *J. Ministry Agr.*, **28** (1921), 308–341; E. P. 152387 (1919); U. S. P. 1471979 (1923).

In purifying cultures of *Spirochæta cytophaga*, there was isolated a new type of aerobic, cellulose-fermenting organism, *Microspira agar-liquefaciens*, that also liquefies agar.[1] The organism appears to enter the fibers and attack the central canal. Certain small quantities of xylose and lignin stimulated fermentation of the cellulose (filter paper). "Straw gum" supported growth but not lignin, xylose, and arabinose. The results are scarcely indicative of the effect of constituents of the natural straw. The lignin must have been modified during isolation; and the straw gum that furnishes xylose did not have a stimulating action.

The thermophilic bacteria are of great interest on account of the speed with which cellulose is decomposed. In 1889, Macfadyen and Blaxall[2] recognized the group of thermophilic bacteria. Viscose was almost completely fermented, at 60°, in 3 weeks, acetic and butyric acids being formed. Failure to ferment pure cellulose with this group may sometimes be due to the absence of iron. Kronlik[3] found that a trace of ferric chloride produced an intense decomposition.

Butyric acid does not appear to be formed by thermophilic bacteria. At 55 to 60°, anaerobic bacteria gave only hydrogen, carbon dioxide, formic acid, and acetic acid, the latter greatly predominating. Fermentation of 3 grams of cellulose gave 0.2125 gram of formic acid and 1.152 grams of acetic acid. The action differs from that of bacteria having an optimum temperature of 37°, since in this case butyric acid is the main product formed.[4] In a methane fermentation of filter paper, De Coninck[5] obtained a small amount of propionic acid, in addition to acetic and butyric acids.

Ruminants are able to digest cellulose by means of the bacteria in the intestinal flora. The excrement of these animals is one of the principal sources for obtaining cultures of thermophilic bacteria.

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[1] P. H. Gray and C. H. Chalmers, *Ann. Appl. Biol.*, **11** (1924), 324–338.

[2] A. Macfadyen and F. R. Blaxall, *Trans. Jenner Inst.*, **II** (1899), 182–185.

[3] A. Kronlik, *Centr. Bakt.*, *Parasitenk.*, II Abt., **36** (1912), 345.

[4] H. Pringsheim, *Centr. Bakt.*, *Parasitenk.*, II Abt., **38** (1913), 513–516.

[5] W. O. deConinck, *Compt. rend. soc. biol.*, **79** (1916), 156–157.

Pringsheim[1] found that the decomposition of cellulose proceeds in the same way with all groups, but is best observed with thermophilic bacteria, with which a fairly strong reduction of Fehling's solution can be observed after 24 hours' action. He was able to show definitely that the cellulose is first hydrolyzed to cellobiose by the enzyme cellulase, and then to glucose by cellobiase. It was found that the vital activity of the bacteria could be destroyed by the use of antiseptics, without affecting the activity of the enzymes, and that the action of the latter was independent of the optimum temperature (55°) of the bacteria. If a vigorous fermentation is removed from the oven at 55°, and held at 20°, glucose is formed; if held at 67°, near the death point of the cellulase, cellobiose is obtained.

Ivory nut fermented with soil bacteria gave a trisaccharide resolved by emulsin into a mono- and disaccharide.[2]

It is assumed that fungi capable of attacking cellulose contain the enzyme cellulase.[3] So far, it has been impossible to isolate an enzyme that will attack cellulose, though hemicelluloses may be broken down by expressed juices. The juice of *Merulius lacrymans* attacks cellulose dextrins.[4]

Hemicelluloses are rapidly dissolved by the expressed juice of the snail, *Helix pomatia*, but cotton and filter paper are not affected.[5] The juice is so completely inactive towards lignified tissues that it is suggested as a reagent for detecting lignification. Cellulose that has been gelatinized by cuprammonium solution, zinc chloride,[6] or 25 per cent potassium hydroxide,[7] is rapidly hydrolyzed to glucose by the juice of this snail. Digestion of this modified cellulose is greatly retarded by drying it in a vacuum. Cherry gum was not attacked by the juice, even after solution in cuprammonium solution. The juice of *H. pomatia* completely dissolved crystalline cellulose, deposited from cuprammonium solution, in 36 hours.[8]

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[1] H. Pringsheim, *Z. physiol. Chem.*, **78** (1912), 266–291.

[2] H. Pringsheim, *Z. physiol. Chem.*, **80** (1912), 376–382.

[3] C. van Iterson, Jun., *Centr. Bakt., Parasitenk.*, II Abt., **11** (1904), 689.

[4] H. Euler, *Z. angew. Chem.*, **25** (1912), 250.

[5] W. Biedermann and P. Moritz, *Arch. Physiol.*, **73** (1898), 266, 267.

[6] G. Seillière, *Compt. rend. soc. biol.*, **63** (1907), 515–517.

[7] G. Seillière, *Compt. rend. soc. biol.*, **68** (1910), 107–109.

[8] J. S. Alexandrowicz, *Arch. Physiol.*, **150** (1913), 69.

Certain enzymes appear to have a slight effect on cellulose. Cotton subjected to the action of saliva for 20 minutes took up nearly double the amount of dyestuff as ordinary cotton.[1] The enzyme pytalin present in the saliva may cause partial gelatinization of the cellulose.

According to Scheurer,[2] cotton is reduced in strength 7 per cent by four successive treatments of 2 hours each, at 60°, in a bath containing 12.5 grams of malt per liter. Reinitzer[3] could not find that any solution of cotton or filter paper took place with malt extract.

Cellulose that has been gelatinized by precipitation from cuprammonium solution is converted into dextrose to the extent of 50 per cent by lichenase, and quantitatively by repeating the treatments.[4] The resolution of the gelatinized cellulose is apparently due to dispersion of the compact, oriented arrangement of the micellæ as found in normal cellulose.

A bacteria-free filtrate from a vigorous thermophilic bacterium was without action on cellulose. To secure fermentation, it is necessary that the bacteria be in direct contact with the cellulose. For these reasons, Pringsheim[5] considers cellulose to be an endoenzyme (acting within the cell), while Löhnis and Lochhead[6] call it an ectoenzyme (capable of traversing the cell membrane). Langwell[7] found that cellulose fermentations of a volume of 8000 liters could be completely stopped by vigorous stirring with a paddle. Every microbe was completely disintegrated to a gelatinous mass, but it is improbable that the accompanying enzyme was destroyed by this treatment.

The probable course of the final steps in the fermentation of cellulose may be traced from the work of Buchner and Meisenheimer.[8] Lactic acid is first formed from the glucose, formation of lactic acid being apparently the first step in alcoholic and butyric acid fermentation. The end products of the fermentation of glucose by *Bacillus butylicus* Fitz are: ethyl alcohol, butyl alcohol, formic acid, acetic acid, lactic acid, *n*-butyric acid, carbon dioxide, and hydrogen. The initial step is hydrolysis of the cellulose:

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[1] E. Knecht, *J. Soc. Dyers Colourists*, **21** (1905), 189–190.

[2] A. Scheurer, *Bull. Mulhouse*, **73** (1903), 320.

[3] F. Reinitzer, *Z. physiol. Chem.*, **23** (1897), 175.

[4] P. Karrer, *Z. angew. Chem.*, **37** (1924), 1003.

[5] H. Pringsheim, *Z. physiol. Chem.*, **78** (1912), 266.

[6] F. Löhnis and G. Lochhead, *Centr. Bakt., Parasitenk.*, II Abt., **58** (1923), 431.

[7] H. Langwell, *J. Soc. Chem. Ind.*, **42** (1923), 287T.

[8] E. Buchner and J. Meisenheimer, *Ber.*, **41** (1908), 1410–1419.

$$\underset{\text{Cellulose}}{(C_6H_{10}O_5)n} \rightarrow \underset{\text{Cellobiose}}{nC_{12}H_{22}O_{11}} \rightarrow \underset{\text{Glucose}}{nC_6H_{12}O_6}.$$

The lactic acid formed from the glucose may undergo the following reactions:

1. $\underset{\text{Lactic acid}}{CH_3.CHOH.COOH} \rightarrow \underset{\text{Formic acid}}{H.COOH} + \underset{\text{Acetaldehyde}}{CH_3.CHO}.$
2. $H.COOH \rightarrow H_2 + CO_2.$
3. $CH_3.CHO + H_2 \rightarrow \underset{\text{Ethyl alcohol}}{CH_3.CH_2OH}.$
4. $2CH_3.CHO \rightarrow \underset{\text{Aldol}}{CH_3.CHOH.CH_2.CHO} \rightarrow \underset{\text{Crotonaldehyde}}{CH_3.CH{:}CH.CHO} + H_2O.$
5. $\underset{\text{Aldol}}{CH_3.CHOH.CH_2.CHO} \rightarrow \underset{n\text{-Butyric acid}}{CH_3.CH_2.CH_2.COOH}.$
6. $\underset{\text{Crotonaldehyde}}{CH_3.CH{:}CH.CHO} + 2H_2 \rightarrow \underset{\text{Butyl alcohol}}{CH_3.CH_2.CH_2.CH_2OH}.$

Buchner suggests that in cellulose fermentations the formic acid probably decomposes into carbon dioxide and hydrogen, and acetic acid into carbon dioxide and methane.

Neuberg and Cohn[1] were able to detect acetaldehyde in the methane and hydrogen fermentation of cellulose at 37°, and at 53 to 55°. They conclude that the fermentations proceed like the butyric acid fermentation, with acetaldehyde as the intermediate product.

Langwell,[2] making extensive use of Neuberg's work[3] on fermentation, gives the following probable steps in the fermentation of cellulose:

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[1] C. Neuberg and R. Cohn, *Biochem. Z.*, **139** (1923), 527–549.

[2] H. Langwell, *J. Soc. Chem. Ind.*, **42** (1923), 280T.

[3] Most of the papers of Neuberg and his associates will be found in the recent volumes of the *Biochemische Zeitschrift.*

1. $\underset{\text{Cellulose}}{C_6H_{10}O_5} + H_2O \rightarrow \underset{\text{Pyruvic acid}}{2CH_3.CO.COOH} + 2H_2.$
2. $CH_3.CO.COOH + H_2 \rightarrow \underset{\text{Lactic acid}}{CH_3.CHOH.COOH}$, or
3. $CH_3.CO.COOH \rightarrow CH_3.CHO + CO_2.$
4. $CH_3.CHO + H_2 \rightarrow CH_3.CH_2OH.$
5. $2CH_3.CHO + H_2O \rightarrow CH_3.CH_2OH + CH_3.COOH.$
6. $2CH_3.CH_2OH \rightarrow CH_3.COOH + 2CH_4.$
7. $2CH_3.CHOH.COOH \rightarrow CH_3.CH_2.CH_2.COOH + 2CO_2 + 2H_2.$
8. $C_6H_{10}O_5 + H_2O \rightarrow 3CH_3.COOH.$

According to Söhngen,[1] the methane produced by bacteria is formed by reduction of carbon dioxide through absorption of hydrogen. Support for this view was found in the formation of

$$CO_2 + 4H_2 = CH_4 + 2H_2O.$$

methane by bacteria grown in an inorganic medium containing carbon dioxide and hydrogen. Under aerobic conditions, an organism, *B. methanicus,* had the power to use methane as its sole source of carbon.

Certain bacteria have the power of synthesizing a carbohydrate closely related to, if not identical with cellulose. The *Bacterium xylinum* of Brown[2] converts lævulose and other sugars into a leathery membrane which in the fresh or purified condition is soluble in cuprammonium solution. The membrane is insoluble in dilute alkalis, and gives a blue color with zinc chloriodine reagent.[3] When grown on sucrose, the organism converts about 7 per cent of the sugar into cellulose.

The sorbose bacterium of Bertrand[4] is identical with *Bacterium xylinum.* When grown in a nitrogenous medium such as beer, it forms a membrane containing chitin as well as cellulose. The membrane contains 2 to 3 per cent of nitrogen and is only slightly soluble in cuprammonium solution.[5] Cellulose and chitin have been reported as constituents of the cell wall of numerous bacteria. The presence of cellulose in *Bacterium xylinum* and *Sarcina ventriculi* has been fairly well established.[1]

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[1] N. L. Söhngen, *Rec. trav. chim.,* **29** (1910), 238.

[2] A. J. Brown, *J. Chem. Soc.,* **49** (1886), 432–439.

[3] C. A. Browne, *J. Am. Chem. Soc.,* **28** (1906), 453.

[4] G. Bertrand, *Bull. soc. chim.,* [3] **15** (1896), 627.

[5] O. Emmerling, *Ber.,* **32** (1899), 541–542.

The cellulose of bacteria does not appear to have been subjected to acetolysis, as has animal cellulose (tunicin) from *Ascidioidea* and *Tunicata.* Aberhalden and Zemplén[2] obtained cellobiose octacetate from the tunicin of *Phallusia mamillaris.*

Wood, while readily attacked by filamentous fungi, is practically unaffected by bacteria. The aqueous extract is too acid to support their growth unless neutralized with calcium carbonate. Even in decayed wood, bacteria appear to be present only in traces.[3]

The wood of trees is normally free from bacteria. When injected into living wood, bacteria remained alive for 10 months but showed no development. After wood has been attacked by filamentous fungi, bacteria may be found, but the two do not occur simultaneously.[4] The freedom of wood from bacteria may be due to tannins that, while supporting the growth of molds, is very toxic to most bacteria.

Sawdust inhibits ammonia and nitrate accumulation in the soil.[5] Cedar sawdust is most inhibitory to ammonia accumulation and white pine least. Cedar, maple, ash, and red fir sawdust had great inhibitory action on nitrate formation.

Lignin prepared from pine wood by heating it with sodium hydroxide under pressure, and containing about 6 per cent of pentosans, was fermented with a bacterial culture from soil.[6] The pentosans were almost completely destroyed. About half of the fermented lignin was soluble in alcohol, the soluble portion being richer in carbon and poorer in methoxyl than the original.

Some attempts have been made to utilize the gas from the methane and hydrogen fermentation of cellulose for fuel purposes. In some English experiments,[7] it was found that 34 per cent of the calorific value of straw could be obtained in the form of combustible gases. Methane fermentation proceeded about 13 times more rapidly than hydrogen fermentation, each requiring special conditions. For methane fermentation, neutrality must be maintained with calcium carbonate, while for hydrogen fermentation, a certain acidity is necessary. In the latter case, the hydrogen-ion concentration can vary only between narrow limits.

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[1] C. van Wisselingh, *Pharm. Weekblad,* **53** (1916), 1069, 1102.

[2] A. Aberhalden and G. Zemplén, *Z. physiol. Chem.,* **72** (1911), 58.

[3] B. Malenkovic, *Z. landw. Versuchs. Oesterr.,* **8** (1905), 852–860.

[4] E. Berthold, *Jahrb. wiss. Botanik,* **57** (1917), 387–458.

[5] W. M. Gibbs and C. H. Werkman, *Soil Science,* **13** (1922), 303–322.

[6] H. Pringsheim and W. Fuchs, *Ber.,* **56** (1923), 2095–2097.

[7] J. Russell, *J. Soc. Chem. Ind.,* **42** (1923), 169T.

The fermentation of various plant wastes was studied by Fowler and Joshi,[1] who used organisms from the sludge of a septic tank. Hemicelluloses were most readily attacked, followed by cellulose from lignified tissues, and normal cellulose. The gas formed daily had a volume equal to 80 per cent of the volume of the fermenting material, and contained 80 to 85 per cent of methane. With the hemicelluloses, acetic but no butyric acid was obtained.

The industrial possibilities of the fermentation of cellulose have been especially investigated by Langwell.[2] The character of the fermentation products is considerably influenced by the degree of aeration; with limited aeration, acetic acid is the chief product, with increased aeration, ethyl alcohol.

The Langwell[3] organism requires about 5 days to ferment the resistant celluloses, the optimum temperature being 60 to 68°. The extent to which the celluloses are destroyed, and the products of fermentation, are shown below.

Cellulose used	Time of fermentation, days	Insoluble organic residue, per cent
Bleached cotton waste	15	8.0
Sulphite pulp	9	9.3
Sulphite pulp	15	8.1
Sulphite pulp	5	15.0
Whatman filter paper No. 40	5	7.0

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[1] G. J. Fowler and G. V. Joshi, *J. Indian Inst. Sci.*, **3,** IV (1920), 39–60.

[2] H. Langwell, U. S. P. 1443881 (1923); Power-Gas Corporation and H. Langwell, E. P., 134265 (1918) and 161294 (1920).

[3] A. H. Lymn and H. Langwell, *J. Soc. Chem. Ind.*, **42** (1923), 280T.

PRODUCTS OF FERMENTATION

Products	Sulphite pulp				Filter paper, per cent	Rice-straw cellulose, per cent
	I, per cent	II, per cent	III, per cent	IV, per cent		
Acetic acid	31.8	59.4	35.1	28.2	43.0	66.2
Butyric acid	....	....	28.6			
Lactic acid	....	....	4.8	45.1	36.6	
Alcohol	27.6	....	2.2	12.9	8.3	0.5
CO_2	42.4	49.5	....	....	....	47.5
H_2	1.0	0.7	....	....	....	0.4
CH_4	0.2	7.6	....	....	....	7.2

Lignocelluloses are scarcely attacked, while sugars, starches, and hemicelluloses behave like cellulose.

Fermentation of Cellulose by Filamentous Fungi.—Confusion has existed regarding the power of fungi to ferment normal cellulose, owing to the loose application of the term "cellulose" to modified celluloses and hemicelluloses. Schellenberg,[1] using various species of *Mucor*, *Penicillium*, and *Botrytis* on cotton and linen, was unable to observe decomposition. The fungi, however, readily attacked various hemicelluloses. Their action was specific, indicating that there are distinct kinds of hemicelluloses requiring particular enzymes. An aqueous extract of *Glomerella cingulata* contained an enzyme capable of splitting xylan.[2] Xylose was isolated in the crystalline form.

Raw cotton stored in a damp condition is seriously weakened by fungi.[3] McBeth and Scales[4] tested numerous species of fungi, principally *Penicillium* and *Aspergillus*, and found that in nearly every case they were able to decompose cellulose. One of the most active cellulose-destroying fungi, *Penicillium pino-*

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[1] H. C. SCHELLENBERG, *Flora*, **98** (1908), 257–308.

[2] L. A. HAWKINS, *Am. J. Botany*, **2** (1915), 375–388.

[3] A. HOLLE, *Chem. Ztg.*, **22** (1898), 824; *Z. Farben-u. Textilchem.*, **4** (1905), 144.

[4] I. G. MCBETH and F. M. SCALES, *Bur. of Plant Ind. Bull.*, **266** (1913); F. M. SCALES, *Botan. Gaz.*, **60** (1915), 149–153.

philum, contained the enzymes sucrase, emulsin, amidase, diastase, catalase, and lipase.[1] Carbone[2] isolated from damaged cotton two species of *Penicillium* that were able to decompose purified cotton.

Ability to dissolve cellulose is shown by *Rhizoctonia solani, Tricothecium roseum,* and numerous species of *Fusarium.*[3] None of the organisms tried dissolved the hemicelluloses, vegetable ivory and date palm (*Phoenix dactylifera*). Molds of the genus *Cladosporium,* in 256 days, destroyed 25 per cent of the cellulose employed.[4]

Certain *Actinomyces,* a border group between bacteria and fungi, are able to attack cellulose, particularly the gelatinized form.[5]

Fermentation of Wood by Filamentous Fungi.—Wood that has undergone decay shows especially a decrease in carbohydrates and greatly increased solubility in water and alkalis. The early discovery of the solubility of decayed wood led to the isolation of numerous substances now classed as humic acids. Crenic and apocrenic acids, previously described by Berzelius from certain spring waters, were reported as present in an old wooden pump.[6] Ulmic acid (ulmin) was so-called from its isolation from the bark of a diseased elm (*Ulmus nigra*).[7] The nitrolin of Hermann[8] and the xylinic acid of Lefort[9] were obtained from decayed wood and considered to be definite compounds.

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[1] E. D. Clark and F. M. Scales, *Proc. Am. Soc. Biol. Chem.* (December, 1915), 31–32; C. A., **10** (1916), 1204.

[2] D. Carbone, *Zentr. Biochem. Biophysk.*, **12** (1912), 821.

[3] F. Heller, "Untersuchungen über Zelluloseabbau durch Pilze," Diss. Rostock (1917), 48 pp.; *cf.* H. Otto, Diss. Berlin (1916), 42 pp.

[4] N. I. Kosin, *Chem. Zentr.*, **93,** III (1922), 874.

[5] A. Kraainsky, *Centr. Bakt., Parasitenk.*, II Abt., **41** (1914), 649; F. M. Scales, *Botan. Gaz.*, **60** (1915), 152.

[6] Winkler, *Jahresber. Chemie,* (1850), 392.

[7] O. M. R. Klaproth, *Gehlen's allgem. J. der Chemie,* **4** (1804), 329; *cf.* L. N. Vauquelin, *Ann. chim. phys.*, [1] **21** (1797), 39–47.

[8] R. Hermann, *J. prakt. Chem.*, **22** (1841), 65–81; **27** (1842), 171; G. J. Mulder, *Ibid.*, **23** (1841), 375–386; *cf. Ibid.*, **21** (1840), 203–240, 321–370; **27** (1842), 165–177.

[9] J. Lefort, *Compt. rend.*, **64** (1867), 1235.

Lettenmeyer and Liebermann[1] obtained from a decayed beech stump the water-soluble ammonium, potassium, and sodium salts of a humic acid. The acid in the dry state contained 53.6 per cent of carbon and 4.9 per cent of hydrogen. It was difficultly soluble in alkalis and insoluble in water, alcohol, and acetic acid. In spite of the large amount of research[2] on the humic acids, it may be safely stated that no chemically individual compounds have yet been isolated.

Humin and humic acids are dark-colored colloidal substances. Humin swells in alkalis but possesses no characteristic chemical properties. The humic acids are soluble in water, alkalis, and dilute acids, but insoluble in salt solutions. There has been much discussion as to whether humic acids are really acids. Indication of acidity in the presence of neutral salts has been attributed to adsorption of the cation. The reaction of humus substances with alkalis has also been classed as an adsorption phenomenon. Odén[3] believes that true humic acids exist. Little is known of their constitution. According to Marcusson,[4] humic acids consist of condensed furan and benzene rings containing carboxyl groups, and possibly alcoholic and phenolic hydroxyl groups.

Humification is a slow oxidation process accompanied by a relative increase in carbon, and decrease in hydrogen and oxygen. According to Benni,[5] cellulose does not form humus by any natural or artificial process. Colored products obtained, *e.g.*, by the fusing of cellulose with alkalis are not necessarily humus. Plant substances other than cellulose are first oxidized to humin, and finally to carbon and volatile, water-soluble acids. Humic acids may be produced by atmospheric oxidation and by the action of bacteria and fungi.[6] Lignin humifies rapidly at a temperature of 37° and above.

It is common knowledge that wood submerged in deep water remains unchanged for ages. Decay is also slow in wood buried

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[1] T. Lettenmeyer and C. Liebermann, *Ber.*, **7** (1874), 408.

[2] S. Odén, "Die Huminsauren," Dresden (1922), 199 pp.

[3] S. Odén, *l.c.*, p. 82.

[4] J. Marcusson, *Z. angew. Chem.*, **35** (1922), 165–166; *Mitt. Materialprüfungsamt*, **40** (1922), 245–249.

[5] S. Benni, *Z. Naturwiss.*, **69** (1896), 145–176.

[6] A. Trouseff, *Bull. Agr. Intelligence*, **6** (1915), 1453; **7** (1916), 46.

8 to 10 feet below the soil, a depth to which bacteria seldom penetrate. Richards[1] examined oak, presumably 1000 years old, from the bed of the Moksha River, central Russia, and oak, probably dating from the Neolithic period, from Irish bogs. The woods retained their natural characteristics to a large extent. Koch[2] examined an oak piling over 2000 years old taken from a bog in Germany. In comparison with fresh wood, it showed less furfural, but more crude fiber and methoxyl, indicating that only the pentosans were affected. Woods rich in "wood gum" are colored darker by contact with water or soil than coniferous woods.[3] The difference is not explainable on the basis of a high or low tannin or phlobaphene content.

Lignin is the principal source of the natural humic acids,[4] which, in turn, constitute an intermediate stage in the formation of coal.[5] The residue from coniferous wood in peat beds shows the structure of the original wood and consists largely of lignin.[6] The wood found in coal is almost entirely of coniferous origin. White and Thiessen[7] believe that most of the decay was brought about by bacteria, the fungi having played only a subordinate rôle since their spores and hyphæ are only rarely found.

Since no definite evidence has been obtained by oxidation, sulphonation, or nitration that lignin contains a benzene ring, Jonas[8] does not agree that coal is derived from lignin. The presence of benzene derivatives in the distillate from coal, and the formation of benzene polycarboxylic acids by the pressure oxidation of lignin and humic acids,[9] may be explained by the assumption of Marcusson[1] that humic acid and lignin contain a peridifuran ring.

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[1] P. A. E. Richards, *Analyst,* **41** (1916), 169, 303.

[2] W. Koch, Diss. Freiburg (1909), p. 36.

[3] F. Hoppe-Seyler, *Z. physiol. Chem.,* **13** (1889), 84.

[4] E. Erdmann, *Z. angew. Chem.,* **34** (1921), 313; F. Hoppe-Seyler, *l.c.*

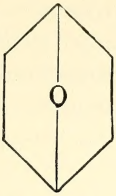
[5] F. Fischer *et al., Brennstoff-Chem.,* **2** (1921), 37–45; **3** (1922), 65–72, 161–167; *Naturwiss.,* **9** (1921), 958–965; *Ges. Abhandl. Kenntnis Kohle,* **5** (1921); **6** (1922).

[6] L. G. de Lamarlière, *Compt. rend.,* **131** (1900), 511–512.

[7] D. White and R. Thiessen, "The Origin of Coal," *Bur. Mines, Bull.,* **38** (1913), 390 pp.

[8] K. G. Jonas, *Z. angew. Chem.,* **34** (1921), 373–374.

[9] F. Fischer and H. Schrader, *Ges. Abhandl. Kenntnis Kohle,* **5** (1921), 221, 311; *Brennstoff-Chem.,* **3** (1922), 161, 341.



Humic acids from decayed oak gave the Procter-Hirst[2] reaction for sulphite liquor and a tannage similar to the later.[3] In the presence of hydrochloric acid, humic acid precipitated tannin from a mixture of tannin and sulphite liquor.[4]

Wagner[5] examined woods that had been attacked by dry rot (*Merulius destruens*), white rot, and red rot. Ultimate analyses showed little difference in composition from the original wood. They were largely soluble in a boiling solution of potassium hydroxide, the wood attacked by dry rot being almost completely so. Oak destroyed to the extent of 74 per cent by *Polyporus ignarius*, aside from loss of starch, sugar, and tannin, did not differ in composition from sound wood.[6]

Analysis of Sound and Decayed Spruce and Oak[7]

	Decayed		Sound	
	Spruce, per cent	Oak, per cent	Spruce, per cent	Oak, per cent
Ash	1.38	4.89		
N	0.49	1.66		
C	52.19	48.31		
H	5.02	3.64		
Pentosan	3.42	4.22	10.03	20.18
Methylpentosan	3.61	2.40	4.70	5.55
Methoxyl	3.49	2.96		

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[1] J. Marcusson, *Z. angew. Chem.*, **36** (1923), 42–43.

[2] H. R. Procter and S. Hirst, *J. Soc. Chem. Ind.*, **28** (1909), 293.

[3] W. Moeller, *Collegium* (1916), 330, 356.

[4] W. Moeller, *Collegium* (1916), 385.

[5] A. Wagner, *Dinglers polytech- J.*, **249** (1883), 342.

[6] R. Hasenöhrl and J. Zellner, *Monatsh.*, **43** (1922), 38.

[7] E. Michelet and J. Sebelien, *Chem. Ztg.*, 30 (1906), 357–358.

A distinct loss of cellulose and pentosans by decay was observed in beech wood.[1] Decayed spruce and oak showed loss of pentosans and so-called methylpentosans.[2]

Spruce (*Picea excelsa*) decayed by *Merulius lacrymans* and the humus bodies extracted therefrom have been examined by Wehmer.[3] The apparent acidity of the decayed wood was attributed to adsorption of alkali and not to free organic acids.

Substance	C, per cent	H, per cent	O, per cent
Sound wood	51.5	8.4	40.1
Decayed wood	56.8	7.1	36.0
Decayed wood:			
Humin I	46.4	6.0	47.5
Humin II	51.6	5.6	42.8
Humin III	64.1	8.0	28.0
Residue	60.5	9.4	30.1

The first complete examination of decayed wood was made by Rose and Lisse.[4] Unfortunately, the fungus that produced the decay was not identified. There was marked increase in solubility in alkali and decrease in cellulose, pentosans, and acetyl groups, while the methoxyl content increased.

A portion of the methoxyl is very resistant. The presence of 0.0 to 1.114 per cent of methoxyl in soils is probably due to lignified tissues.[5] The increase or decrease in methoxyl may be due to a difference in the fungi. Fischer[6] and his associates observed a loss of methoxyl. Mahood and Cable[7] obtained a slight increase in methoxyl, an increase in lignin, and a decrease in cellulose and pentosans in infected ground-wood pulp. In this case the differences between the sound and infected wood were not marked.

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[1] F. H. Storer, *Bull. Bussey Inst.*, **2** (1897), 410.

[2] E. Michelet and J. Sebelien, *Chem. Ztg.*, **30** (1906), 357–358.

[3] C. Wehmer, *Ber.*, **48** (1915), 130–134.

[4] R. E. Rose and M. W. Lisse, *J. Ind. Eng. Chem.*, **9** (1917), 284.

[5] E. C. Shorey and E. C. Lathrop, *J. Am. Chem. Soc.*, **33** (1911), 75–78

[6] F. Fischer, H. Schrader, and A. Friedrich, *Ges. Abhandl. Kenntnis Kohle*, **5** (1920), 530, 553.

[7] S. A. Mahood and D. E. Cable, *Paper*, **25**, 24 (1920) 11.

ANALYSIS OF SOUND AND DECAYED DOUGLAS FIR[1]

	Sound heartwood, per cent	Partial rot, per cent	Complete rot, per cent
Cold-water-soluble	4.03	1.75	1.16
Hot-water-soluble*	2.23	4.19	7.77
Alkali-soluble	10.61	38.10	65.31
Cellulose	58.96	41.66	8.47
Acetic acid by hydrolysis	0.71	0.28	0.17
Pentosan	7.16	6.79	2.96
Methylpentosan	2.64	3.56	6.06
Methoxyl	3.94	5.16	7.80
Moisture	9.81	10.63	9.09
Ether extract	2.71	2.05	2.72
Ash	0.15	0.15	0.65

* Less cold-water-soluble.

[1] R. E. ROSE and M. W. LISSE, *l.c.*

The decay of round-wood and mechanical pulp during storage is frequently a serious economic problem. Cross and Bevan[1] found that baled mechanical pulp, affected by "heart" damage, had increased in solubility in water, from 1.8 to 20.0 per cent. As high as 24 per cent of water-soluble constituents having a strong cupric reducing power have been observed in damaged pulp.[2] The loss by decay of round pulp wood may attain 75 per cent in a year.[3] Wood so decayed showed a loss of 76 per cent of cellulose, 80 per cent of acetyl groups, 77 per cent of pentosan, and 65 per cent of methylpentosan.

Infected ground-wood pulp shows great decrease in fiber length, great "freeness" on the paper machine, a darker color, and a decided reduction in the strength of the finished paper.[4] Furthermore, a greatly increased consumption of chemicals is required in cooking decayed wood by alkaline pulping processes, since the usual quantity of alkali is quickly neutralized by the humic acids.[1] Sulphite pulp from decayed wood is very difficult to bleach and the yield and the strength are greatly reduced.[2]

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[1] C. F. CROSS and E. J. BEVAN, *J. Soc. Chem. Ind.*, **27** (1908), 1188.

[2] F. BARNES, *Pulp Paper Mag. Can.*, **10** (1912), 80.

[3] S. F. ACREE, *Pulp Paper Mag. Can.*, **17** (1919), 569–571.

[4] O. KRESS, C. J. HUMPHREY, and C. A. RICHARDS, *Paper Ind.*, **1** (1919), 526–531; O. KRESS and C. J. HUMPHREY, *Paper Trade J.*, (Nov. 18, 1920).

To prevent the discoloration of pulp by molds, Herzberg[3] recommended a dilute solution of zinc chloride. Zinc chloride and mercuric chloride are not as satisfactory as sodium fluoride, applied in a 1 per cent solution, so as to give 0.58 per cent of salt on the air-dry pulp.[4]

Very slight deterioration of mechanical pulp takes place at a temperature of 1 to 2°, or when stored in clean water.[5] The fungi commonly found on pulp logs will not, as a rule, penetrate the wood if its moisture content is below the fiber saturation point (20 to 30 per cent) or above 60 per cent.[6] Greatest growth takes place between these limits.

As shown by Bray and Staidl,[7] the decrease in α-cellulose is the most prominent characteristic of the decay of ground-wood. The β-cellulose is greatly increased while the γ-cellulose decreases. The lignin remains practically constant when the weight of the wood is considered. Ground-wood, consisting of 70 per cent spruce and 30 per cent balsam, when inoculated with various species of hymenomycetes, lost 10.3 to 27.2 per cent by weight after 6 months.[8] One culture showed a loss of 49.5 per cent after 1 year, and 62.4 per cent after 3 years. At the end of 6, 12, and 36 months the cellulose contents were 26.8, 10.9, and 6.05 per cent respectively.

Ward[9] observed that molds such as *Penicillium* were more active destroyers of wood than had hitherto been supposed. With spruce, the starch cells of the medullary rays of the sapwood were first attacked. The hyphæ after 3 months had penetrated the wood deeply, passing from tracheid to tracheid through the bordered pits.

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[1] E. Sutermeister, *Pulp Paper Mag. Can.*, **19** (1921), 733.

[2] E. Sutermeister, *Pulp Paper Mag. Can.*, **20** (1922), 513.

[3] W. Herzberg, *J. Soc. Chem. Ind.*, **8** (1889), 702.

[4] J. S. Bates, *Pulp Paper Mag. Can.*, **19** (1921), 581–583; O. Kress *et al.*, "Control of Decay in Pulp and Pulp Wood," *U. S. Dept. Agr. Bull.*, **1298** (1925), 80 pp.

[5] R. J. Blair and E. Parke-Cameron, *Pulp Paper Mag. Can.*, **20** (1922), 64–67.

[6] W. H. Snell, *Pulp Paper Mag. Can.*, **19** (1921), 531–533.

[7] M. W. Bray and J. A. Staidl, *J. Ind. Eng. Chem.*, **14** (1922), 35–40; *cf.* O. Kress, *Pulp Paper Mag. Can.*, **18** (1920), 1225–1229.

[8] M. W. Bray and T. M. Andrews, *J. Ind. Eng. Chem.*, **16** (1924), 137–139.

[9] H. M. Ward, *Ann. Botany*, **12** (1898), 565–566.

Various fungi are alleged to act specifically on lignin or carbohydrates.[1] Hartig[2] states that *Polyporus vaporarius*, *P. sulphureus*, and *Merulius lacrymans* remove the cellulose, leaving wood gum, while *Trametes pini* removes the lignin, leaving pure cellulose. After loss of the lignin, the middle lamella dissolves leaving isolated tracheids. This is obviously incorrect, since we now know that the middle lamella consists largely of lignin.

The contention of Hartig and most subsequent investigators that the residue of decay consists of pure cellulose, is based on staining with zinc chloriodine solution. This is an unsafe criterion. Lindroth[3] observed that, with birch attacked by *Polyporus*, the phloroglucinol reaction for lignin first disappears, then the Mäule reaction. As the phloroglucinol reaction disappears, the cellulose reaction becomes more intense, until it indicates pure cellulose. Von Schrenk[4] states that *Polyporus juniperus* removes the lignin from red cedar, while *Polyporus carneus* removes the cellulose completely. He[5] further states that *Polyporus fraxinophilus* produces delignification of white ash wood, as shown by color reactions, but the white residue is not pure cellulose, since the fibers stain yellow-brown, not blue, with iodine reagent. This is true also of the white fibers produced by the action of various species of fungi on hardwoods.

According to Johnsen and Lee,[6] decay of wood by *Trametes pini* caused an increase of 15 per cent in cellulose and a decrease of 30 per cent in lignin. Oak attacked by *Thelophora perdix* showed an increase in cellulose as determined with nitric acid and potassium chlorate.[7] Sound and decayed wood contained 47.18 and 68.66 per cent of cellulose respectively.

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[1] E. E. Hubert, *J. Agr. Research*, **29** (1924), 526.

[2] R. Hartig, "Lehrbuch der Pflanzenkrankheiten," 3d ed., Berlin (1900), 173, 177, 178; *cf.* "Die Zersetzungserscheinungen des Holzes der Nadelholzbäume und der Eiche," Berlin (1878), 151.

[3] I. Lindroth, *Z. Land-u. Forstwirts.*, **2** (1904), 393–406.

[4] H. von Schrenk, *U. S. Dept. Agr., Div. of Veg. Physiol. and Path., Bull.*, **21** (1900).

[5] H. von Schrenk, *Bur. of Plant Ind. Bull.*, **32** (1903).

[6] B. Johnsen and H. N. Lee, *Chem. Met. Eng.*, **28** (1923), 258.

[7] Helbig, *Naturwiss. Z. Forst-u. Landw.*, **9** (1911), 246–250.

It has been shown that *Merulius lacrymans* and various hymenomycetes rapidly attack wood gum.[1] The pentosans of wood are rapidly attacked in the soil by various species of *Aspergillus* and *Penicillium.*[2] In 6 months, the pentosans of poplar, birch, and alder were destroyed to the extent of 69, 60, and 47 per cent respectively. The cellulose disappeared much less rapidly. Wood is destroyed in soil principally by hyphomycetes.[3]

Statements have been made that decayed wood retains a certain amount of pentosans; so it should be mentioned that the mycelia of wood fungi contain pentosans. Wichers and Tollens[4] found pentosans ranging from 1.2 per cent in *Xylaria polymorpha* to 6.5 per cent in *Lenzites flaccida;* the fungi *Penicillium glaucum* and *Aspergillus niger* contain 0.86 to 1.17 per cent.[5] Fungi examined by Ishida and Tollens[6] contained 2.6 to 5.1 per cent pentosans and 1.0 to 2.2 per cent methylpentosans. The pentosan content of *Aspergillus* and *Penicillium* is normally about 0.9 per cent, but if the fungi are grown in a medium containing xylose, this value is increased to about 1.4 per cent.[7]

Wood-destroying fungi are rich in enzymes, a dozen having been reported from a single species.[8] Czapek[9] observed that greatly increased quantities of "hadromal" could be extracted from woods that had been attacked by fungi, and assumed that they contained an enzyme, "hadromase," capable of splitting the ether linkage between cellulose and hadromal. Wood, incubated with extracts of fungi for 2 weeks, gave a greatly increased hadromal extract and the wood was colored purple with iodine reagent. Hadromase was obtained by von Schrenk[1] from the mycelia of *Polyporus subacidus* growing in spruce wood. An enzyme extract of *Lenzites sæpiaria* was prepared by Zeller.[2] After allowing the extract to act on the sapwood of *Pinus echinata*, an alcohol extract was obtained that gave the phloroglucinol reaction. He proposes the name "ligninase" for Czapek's hadromase.

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[1] J. Schorstein, *Zentr. Bakt., Parasitenk.*, II Abt., **9** (1902), 446–447.

[2] E. G. Schmidt, W. H. Peterson, and E. B. Fred, *Soil Science,* **15** (1923), 479–488.

[3] B. Majmone, *Chem. Zentr.*, **80,** II (1909), 1074.

[4] J. L. Wichers and B. Tollens, *J. Landw.*, **58** (1910), 238–242.

[5] A. W. Dox and R. E. Neidig, *J. Biol. Chem.*, **9** (1911), 267–269.

[6] M. Ishida and B. Tollens, *J. Landw.*, **59** (1911), 64.

[7] E. G. Schmidt *et al., l.c.*, 486.

[8] H. Schmitz, *J. Gen. Physiol.*, **2** (1920), 613; *Ibid.*, **3** (1921), 795; S. M. Zeller, *Ann. Missouri Botan. Gardens,* **3** (1916), 439; A. H. Buller, *Ann. Botany,* **20** (1906), 49.

[9] F. Czapek, *Ber. botan. Ges.*, **17** (1899), 166–170.

The reputed removal of lignin from the wood of *Æsculus* by *Stereum hirsutum*, leaving a residue of cellulose, is based on color reactions.[3] No enzyme capable of delignification could be isolated. Hasenöhrl and Zellner[4] examined several wood-destroying fungi and were unable to detect enzymes splitting lignocellulose.

Cellulose-dissolving bacteria are not important in the decay of wood by fungi under natural conditions, though saprophytic bacteria appear materially to increase decay.[5] The influence of bacteria on the rate of decay of wood by fungi varies with the fungus and the species of wood.

In studying the influence of the hydrogen-ion concentration of the medium on the development of the mycelia of wood-destroying fungi, Meacham[6] found that the first marked deflection in the growth curve occurred at an acidity of $N/350$ and was limited by $N/50$. The hydrogen-ion concentration, however, does not appear to be the chief factor determining a desirable medium; at least, no general statement can be made on the relation between the hydrogen-ion concentration of the medium and the growth of wood-destroying fungi.[7]

The acidity of wood attacked by dry rot is due to oxalic acid.[8] According to Petri,[9] the basidomycete, *Coniophora cerebella*, renders wood acid by the formation of potassium acid oxalate.

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[1] H. von Schrenk, *l.c.*, *Bull.*, **21**, 12.

[2] S. M. Zeller, *Ann. Missouri Botan. Gardens*, **3** (1916), 468.

[3] H. M. Ward, *Trans. Roy. Soc.* **189B** (1897), 123–134.

[4] R. Hasenöhrl and J. Zellner, *Monatsh.*, **43** (1922), 36.

[5] H. Schmitz, *Ann. Missouri Botan. Gardens*, **6** (1919), 93–136.

[6] M. R. Meacham, *Science*, **48** (1918), 499–500.

[7] S. M. Zeller, H. Schmitz, and B. M. Duggar, *Ann. Missouri Botan. Gardens*, **6** (1919), 137–142.

[8] C. Wehmer, *Ber. botan. Ges.*, **32** (1914), 601–608.

[9] L. Petri, *Bull. Agr. Intelligence*, **8** (1917), 1431–1432.

The fungus, *Merulius lacrymans*, is very sensitive to gallic and tannic acids.[1] For this reason, it attacks coniferous wood rapidly, but not oak.[2] The growth of this fungus is completely stopped by the presence of 1 to 2 per cent of these acids, so that coniferous wood can be made resistant to *Merulius* by impregnation with tannic acid.

The influence of the physical properties of longleaf, shortleaf, and loblolly pine on decay by *Lenzites sœpiaria* has been studied by Zeller.[3] Durability increases with density, and narrow rings are more durable than broad. The age of the heartwood shows no relation to durability. Sapwood decays irrespective of density, width of annual rings, and resin content, the latter being an unsafe index of durability. Resin is not toxic, since it does not entirely inhibit the growth of the fungus in resin-agar emulsion containing 85 per cent of resin.[4] Aside from offering mechanical resistance to the mycelium, resin reduces the power of the wood to take up water.

Sterilization of wood by heating it with water in an autoclave greatly influences the rate of decay.[5] The decay of western hemlock by *Fomes pinicola* was increased by heating the wood in an autoclave up to 10 hours, while after 20 hours the fungus would not attack the wood. The latter had evidently undergone some change that rendered it toxic.

There has been much speculation, but little experimental work, whereby woods can be classified as to durability on the basis of their chemical composition. Payen,[6] in 1844, attributed the resistance of acacia to decay to the thickness of its fibers and the smaller amount of incrusting substances. Occasional attempts have been made to correlate durability with the substances extractable with water and organic solvents. Potter[7] observed that the solution obtained by boiling the sapwood of oak wood in water supported the growth of *Bacillus subtilis;* since a similar extract from the heartwood was less favorable to bacterial growth, he concluded that the durability of heartwood was due to the different nature of the extract. Hawley and his associates[1] in a very important paper have tested the effect of the hot- and cold-water extractives of various woods on *Fomes annosus,* one of the most resistant of the wood-destroying fungi. The retardation of growth of the fungus by extracts of a concentration of 50 per cent is shown below:

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[1] C. Wehmer, *Mycolog. Centr.*, **1** (1912), 138–148, 166–174.

[2] C. Wehmer, *Ber. botan. Ges.*, **29** (1911), 704–708.

[3] S. M. Zeller, *Ann. Missouri Botan. Gardens*, **4** (1917), 93–164.

[4] S. M. Zeller, *Ann. Missouri Botan. Gardens*, **3** (1916), 451.

[5] H. Schmitz, *Ann. Missouri Botan. Gardens*, **6** (1919), 106.

[6] A. Payen, *Compt. rend.*, **18** (1844), 272.

[7] M. C. Potter, *Ann. Botany*, **18** (1904), 133.

Species	Sapwood				Heartwood			
	Cold-water extract		Hot-water extract		Cold-water extract		Hot-water extract	
	In wood, per cent	Retardation, per cent	In wood, per cent	Retardation, per cent	In wood, per cent	Retardation, per cent	In wood, per cent	Retardation, per cent
Catalpa	4.82	72.0	7.92	91.0	6.46	99.9	9.24	100.0
Red oak	3.57	52.0	6.13	64.0	5.74	72.0	8.29	76.0
Redwood	4.28	41.0	6.50	73.0	10.53	93.0	14.39	100.0
Red alder	4.38	31.0	5.35	29.0	3.97	16.0	5.21	39.0
Red mulberry	9.12	10.0	12.56	89.0	7.08	100.0	10.20	100.0
White oak	4.27	0	5.73	0	4.75	70.0	6.60	100.0
Pacific yew	1.90	....	3.18	57.0	8.25	70.0	10.41	85.0
Black locust	3.08	....	3.91	0	9.29	99.9	11.04	100.0
Honey locust	....	....	....	....	7.93	98.0	10.96	99.9
Black walnut	....	....	....	....	7.71	81.0	10.65	96.0

The more durable woods contain large amounts of usually dark-colored extractives in comparison with small amounts of light-colored extractives for rapidly decaying woods. There is no direct relationship, however, between the amount of extractives and durability. In all cases the sapwood extractive is less toxic than the heartwood extractive, this being in accordance with the relative durability of the two forms of wood. The toxic constituents have yet to be identified.

Woods containing volatile oils and resins are usually quite durable. The volatile oils have a toxic action, while the protection afforded by resin is of a physical nature.

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[1] L. F. Hawley, L. C. Fleck, and C. A. Richards, *J. Ind. Eng. Chem.*, **15** (1924), 699.

Products of Decay.—Few definite products have been isolated from decayed wood. Grüss[1] obtained crystalline copper salts of a lignin acid from decayed oak and pine, the lignin having been converted into the acid presumably by an oxidase in the fungi. Pine wood decayed by *Trametes radiciparda,* and oak destroyed by *Polyporus versicolor,* gave the copper salt of mycolignic acid on boiling with cupric oxide.

A black powder obtained from a hollow in an oak liberated heat on exposure to sunlight. It then contained mellitic acid,[2] which was not present originally.

Lignoceric acid, and probably inactive cerebronic acid, were obtained by the distillation of decayed oak wood.[3] Lignoceric acid, $C_{24}H_{48}O_2$, m.p. 80 to 81°, has also been isolated from plant humus[4] by extraction with alcohol. Though it may be formed by the action of microorganisms on lignified tissues, it is more probable that the acid occurs as such, since it has also been obtained by the distillation of apparently sound wood.

Vanillin[5] has been detected colorimetrically in decayed oak wood.

Characteristic of many of the fungi is the formation of pigments which usually remain in the mycelia, but are sometimes secreted. Wood attacked by fungi may, accordingly, be stained various colors. Hedgcock[6] classifies the chromogenic fungi found on wood as follows:

I. Blue stain:
  1. Ceratostomella.

II. Black and brown stain:
  1. Graphium.
  2. Hormodendron.
  3. Hormiscium.
  4. Other fungi.

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[1] J. Grüss, *Ber. botan. Ges.*, **41** (1923), 48, 53.
[2] E. O. von Lippmann, *Ber.*, **54** (1921), 3111.
[3] M. X. Sullivan, *J. Ind. Eng. Chem.*, **8** (1916), 1027–1028.
[4] O. Schreiner and E. C. Shorey, *J. Am. Chem. Soc.*, **32** (1910), 1679.
[5] M. X. Sullivan, *J. Ind. Eng. Chem.*, **6** (1914), 919.
[6] G. G. Hedgcock, *Report Missouri Botan. Gardens*, **17** (1906), 59–114.

III. Red stain:
  1. Penicillium.
  2. Fusarium.

Group III secretes soluble pigments that are taken up by the adjacent wood cells.

The grayish-olive stain of hardwoods is due to *Lasiosphærie pezizula;*[1] the yellow stain of hardwoods to *Penicillium divaricatum;*[2] and the scorched color of conifers to a species of *Alternaria.*

The blue stain of western yellow pine is produced by *Ceratostomella pilifera.* This fungus enters the medullary rays and is unable to attack lignified tissues. Red rot is produced by *Polyporus ponderosus,* which follows *C. pilifera* and attacks the cellulose.[3]

In 1863, Fordos[4] examined oak wood stained an intense green. Chloroform extracted a green pigment, xylochloeric acid. Acids turned it blue or greenish blue, and a small amount of a red pigment could be washed out with water. Ammonia changed the green pigment into a compound insoluble in chloroform. A similar compound was obtained by Rommier[5] and called "xylindein." The pigment was isolated by extracting the wood with 1 per cent sodium or potassium hydroxide and acidifying with hydrochloric acid. One kilogram of wood gave 60 to 80 grams of pigment. Xylindein is produced by *Heliotum æruginosum* and occurs in the hyphæ of the fungus.[6]

Brooks[7] proposes to color wood by inoculating the sterilized product with pure cultures of chromogenic fungi.

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[1] C. J. Humphrey, *Proc. Am. Wood-Preservers' Assoc.,* **16** (1920), 217–250.

[2] E. E. Hubert, *Hardwood Record,* **52,** 11 (1922), 17–19.

[3] H. von Schrenk, "The 'Bluing' and 'Red Rot' of the Western Yellow Pine," *Bur. of Plant Ind. Bull.,* **36** (1903).

[4] Fordos, *Compt. rend.,* **57** (1863), 50–54.

[5] A. Rommier, *Compt. rend.,* **66** (1868), 108.

[6] P. Vuillemin, *Bull. Soc. Sciences Nancy,* **II,** 15 (1898), 90–145.

[7] F. T. Brooks, E. P. 24595 (1913).

CHAPTER XV

DIGESTION OF CELLULOSE AND WOOD BY ANIMALS

Ruminants are able to digest certain forms of cellulose through the presence of cellulose-dissolving bacteria and fungi in the intestinal tract[1]. It has been impossible to extract cellulose-dissolving enzymes from the walls of the stomach or intestines.[2] Extracts from the first stomach, small intestines, and pancreas of cattle were incapable of splitting even cellulose dextrin.[3] In the paunch of the ox carbohydrates are fermented to methane, carbon dioxide, and fatty acids. Hydrogen is never found.[4] The $\frac{CO_2}{CH_4}$ ratio is 2.6. It is not unusual for a cow to produce 0.7 cubic meter of methane in a day. While the nutritive value of cellulose has its origin mainly in the fatty acids produced, the statement of Lusk[5] that dextrose is not formed in the digestion of cellulose is subject to correction in view of the work of Pringsheim.[6]

During the past quarter century numerous experiments have been conducted in feeding animals not only raw straw and wood, but especially the residues obtained by subjecting the compound celluloses to a more or less drastic treatment with alkalis and acids. Lehmann,[7] in 1900, showed that cattle digested 88 per cent of the organic matter of straw pulp, as prepared for the manufacture of paper. Experiments made in Sweden and Germany during the war showed that wood and straw pulps, prepared by the usual chemical processes, had a coefficient of digestibility of 85 to 95 per cent,[1] and was a satisfactory substitute for fodder for both horses and cattle. Wood pulp was utilized as efficiently as straw pulp by sheep.[2] Soda wood pulp analyzed by the customary agricultural methods had the following composition:

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[1] H. Tappeiner, *Z. Biol.*, **24** (1888), 105; A. Scheunert, *Z. physiol. Chem.*, **48** (1906), 14; H. von Hoesslin and E. J. Lesser, *Z. Biol.*, **54** (1910), 47.

[2] W. Ellenberger *et al.*, *Z. physiol. Chem.*, **96** (1915), 236.

[3] H. Pringsheim and A. M. von Merkatz, *Z. physiol. Chem.*, **105** (1919), 173.

[4] A. Krogh and H. O. Schmit-Jensen, *Biochem. J.*, **14** (1920), 686.

[5] G. Lusk, *Am. J. Physiol.*, **27** (1911), 467–468.

[6] H. Pringsheim, *Z. physiol. Chem.*, **78** (1912), 266.

[7] F. Lehmann *et al.*, *Landw. Vers.-Sta.*, **53** (1900), 302.

	Per Cent		Per Cent
Organic matter	99.17	Ether extract	0.17
Nitrogenous matter	0.42	Crude fiber	86.56
Nitrogen-free extract	12.02	Ash	0.83

The pulp formed 22.5 per cent of a mixed ration, including hay, linseed-oil cake, and salt. Of the crude fiber, 89.0 to 96.0 per cent was digested in the case of sulphite pulp; 88.7 per cent of soda pulp; and 97.5 per cent of a severely cooked soda pulp.

The lignin in straw is much more susceptible to the action of alkalis than that in wood. This renders it possible greatly to modify the food value of straw by a very mild alkaline treatment. Ordinary straw is digestible to the extent of 32 to 37 per cent. Treatment with alkali gives 55 to 75 per cent of a fodder which is digestible to the extent of 70 to 75 per cent.[3] By the Beckmann[4] method, chopped straw is allowed to digest in the cold with eight times its weight of 1 to 2 per cent sodium hydroxide for 48 hours, and washed. The dissolved portion consists almost entirely of lignin, only a slight amount of xylan being present. In the cold, it is preferable to use eight parts of 1.5 per cent sodium hydroxide, which is equivalent to 12 per cent sodium hydroxide. Since the alkali is only partially exhausted, it may be reused, thus reducing the actual consumption to 8 per cent. A 1 per cent sodium hydroxide solution will also give a suitable fodder at a temperature of 50°. The use of ammonia under pressure, followed by lime, has been protected by Lehmann,[1] while Waentig[2] treats wood first with chlorine, then with dilute alkali. Other methods are based on heating the lignocellulose with sodium hydroxide, sodium carbonate, or lime, at or above atmospheric pressure.

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[1] H. Edin, C. A., **13** (1919), 2942; C. G. Schwalbe, *Papier-Ztg.*, **43** (1918), 318; *J. Soc. Chem. Ind.*, **37** (1918), 437R.

[2] G. Fingerling, *Landw. Vers.-Sta.*, **92** (1918), 147–170; *cf.* W. Ellenberger, *Biedermann's Zentr.*, **46** (1917), 427; **47** (1918), 368; **49** (1920), 27.

[3] H. Magnus, "Theorie und Praxis der Strohaufschliessung," Berlin (1919), 43 pp.

[4] E. Beckmann *et al.*, *Z. angew. Chem.*, **32** (1919), 81–82; G. P. 305641 (1917).

The products suitable for fodder, obtained by treating straw with alkalis, are known as kraft straws (*Kraftstroh*). Their composition and digestibility are given below:[3]

COMPOSITION OF KRAFT STRAWS

		Treatment					
		8 per cent	8 per cent	1.5 per cent	8 per cent	7.3 per cent	8 per cent
Chemical	.....	NaOH	NaOH	NaOH	Na_2CO_3	CaO	CaO
Time, hours	......	4.5	5.5	8	3	4.5	5
Temperature, atmospheres	......	5	1	Cold	1	5	1
	Raw straw	Composition of Product, Per Cent					
Ash	3.8	4.1	5.00	3.1	2.42	6.53	5.46
Crude protein	2.7	0.9	0.94	2.3	2.00	0.92	1.74
Crude fat	2.1	....	.....	1.3			
Pentosans	26.2	31.1	27.90	26.3	27.50	21.35	27.88
Cellulose	39.5	56.3	52.40	48.6	52.03	53.90	45.57
Lignin	24.0	10.0	12.50	16.3	16.99	20.50	19.20
		Loss of Substances					
Yields		53.0	58.0	79.0	74.0	63.0	73.0
Loss of incrustants		20.3	17.3	12.4	14.73	12.1	10.0
Loss of nutritive substances		26.7	24.7	8.6	11.27	24.9	17.0

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[1] F. LEHMANN, G. P. 169880 (1905).

[2] P. WAENTIG, G. P. 349842 (1917).

[3] H. PRINGSHEIM, *Z. angew. Chem.*, **32** (1919), 249–252.

DIGESTIBILITY OF STRAW AND KRAFT STRAWS

Substance	Digestible crude fiber	Digestible nitrogen-free extract	Starch value
Winter straw	25.67	1.52	13.3
Treated straw:			
1. With NaOH under pressure	50.79	21.26	67.82
2. Cooked with NaOH in open vessel	52.79	21.13	68.67
3. Cooked with CaO under pressure	45.14	3.85	40.93
4. Cooked with CaO in open vessel	51.91	11.56	55.26
5. With NaOH in cold	44.93	23.37	63.50

Kraft straw must be fed shortly after its preparation, since if stored in the wet condition it does not keep well, becoming acid. In the dry state it resembles strawboard and is not a satisfactory food.[1] These difficulties may be overcome by mixing it in the wet state with molasses and starchy or nitrogenous products, and then drying.

Pentosans, which form a large part of the hemicelluloses of the cereal straws, are readily digested. The intestinal bacteria of the guinea pig ferment xylan rapidly and produce notable quantities of fatty acids consisting of about eight parts of acetic acid to one of butyric acid.[2] The pentosans of the corn plant disappear more rapidly in the digestive tract of the cow than those of wheat and oat plants, the amounts digested exceeding 50 per cent.[3] The methylpentosans are less resistant than the pentosans.

There are conflicting reports on the ability of the higher animals to digest wood. Kellner[4] fed oxen with a mixture of 2 kilos of fine spruce sawdust, 0.4 kilo of molasses, and 7 kilos of hay. He found that 17.7 per cent of the cellulose and other carbohydrates in the wood had disappeared. Horses were able to digest from 26.8 to 28.8 per cent of Norway spruce meal.[5] The utilization of hydrolyzed wood was scarcely better, being

[1] B. TOLLENS, *J. Landw.*, **65** (1917), 219–232.

[2] G. SEILLIÈRE, *Compt. rend. soc. biol.*, **68** (1910), 991.

[3] E. V. MCCOLLUM and W. A. BRANNON, *J. Am. Chem. Soc.*, **31** (1909), 1252–1260.

[4] O. KELLNER, *Fühlings Landw. Zeit.*, **43** (1894), 344–346.

[5] W. ELLENBERGER and P. WAENTIG, *Deut. Landw. Presse*, **44** (1917), 335, 343, 558.

27.9 to 29.4 per cent. On the other hand, the crude fiber (72.45 per cent) of finely ground sulphite pulp was digested to the extent of 78.6 to 87.0 per cent. Pine-wood meal, after cooking with sodium hydroxide, had so high a degree of utilization that 4.5 kilos could be given to a horse per day.[1]

The extent to which fodders of these types, wood in particular, are utilized depends on the degree of comminution. Haberlandt and Zuntz[2] in feeding experiments conducted with sheep in a respiration calorimeter found that finely ground mechanical pulp from birch wood was digested to a high degree. Of the crude fiber, 50 per cent, and of the non-nitrogenous substances, 56 per cent, were digested. Unless the wood was ground sufficiently to destroy the cells, the middle lamella, which contains most of the lignin, protects the cellulose layers from attack by the digestive enzymes of the bacteria. Furthermore, with substances like wood and straw 85 per cent or more of the energy value of the fodder digested is expended in mastication.

The twigs of beech, aspen, and other trees, unless very young, have a low digestibility.[3] Their food value is less than that of straw. The digestible portions of raw wood are largely limited to starch and hemicelluloses. Lignin, either in its isolated or natural state, is entirely indigestible.[4]

Early in the development of the Classen process for producing ethyl alcohol from wood, the possibility was recognized of using the hydrolyzed product for a stock food. The methods[5] employed do not differ essentially from those used in the manufacture of alcohol. Acid hydrolysis gives about 25 per cent of sugars, while the insoluble, very friable residue consists of lignin and hydrocellulose, the latter presumably in a form more easily digestible than the original cellulose. In practice, increased digestibility has not been obtained. The hydrolyzed wood was mixed with molasses and marketed as "bastol" and "sacchulose." In some cases the sugars formed from the wood were permanently removed.

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[1] W. Ellenberger and P. Waentig, *Deut. Landw. Presse,* **45** (1918), 195.

[2] G. Haberlandt and N. Zuntz, *Chem. Ztg.,* **39** (1915), 861.

[3] A. Gunther *et al., J. Landw.,* **41** (1893), 65–83.

[4] H. Magnus, *l.c.,* pp. 29–32.

[5] A. Classen, G. P. 270363 (1912); A. D. Little, U. S. P. 1092221 (1914); T. B. Walker, U. S. P. 1140138 and 1155531 (1915); V. Raisin, U. S. P. 998858 (1911) and 1021477 (1912).

Honcamp[1] fed both raw sawdust and "bastol" to sheep. The ration containing sawdust showed a minus coefficient of digestibility. In the case of hydrolyzed wood, it was concluded from determination of the crude fiber in the fæces that the hydrolyzed wood was no more digestible than the untreated, even though the sheep showed a gain in weight. Zimmermann,[2] however, maintained, as a result of feeding experiments conducted with work horses over a period of 6 months, that the 4 pounds of oats usually fed could be replaced by an equal weight of "sacchulose." It is also stated by Ellenberger[3] that hydrolyzed wood may replace hay in the ration of work horses and may also replace the oats if another form of protein is substituted.

Experiments have been made at the University of Wisconsin by F. B. Morrison[4] to determine the nutritive value of hydrolyzed wood for dairy cows. The hydrolyzed wood was prepared by Sherrard[5] from mill-run white pine (*Pinus strobus*) sawdust. The compositions of the raw and treated wood are given below. The normal concentrate mixture fed the cows consisted of 55 parts

Composition of Raw and Hydrolyzed White Pine
(Through 100-mesh)

	Moisture, per cent	Soluble in				Acetic acid, per cent	Pentosans, per cent
		Cold water, per cent	Hot water, per cent	Ether, per cent	1 per cent NaOH, per cent		
Raw	6.39	9.22	10.87	4.86	25.57	0.91	9.86
Hydrolyzed	3.88	29.33	28.31	3.93	39.64	0.65	4.66

	Methylpentosan	Cellulose	Lignin	Crude fiber	Reducing sugars	Ash	
Raw	2.83	54.45	30.50	60.81	0	1.51	
Hydrolyzed	2.50	37.90	31.46	49.31	16.20	3.31	

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[1] F. Honcamp *et al.*, *Landw. Vers.-Sta.*, **78** (1912), 87–114.

[2] A. Zimmermann, *J. Roy. Soc. Arts*, **61** (1912), 69–81.

[3] W. Ellenberger, C. A., **15** (1921), 2943.

[4] F. B. Morrison *et al.*, *Proc. Am. Soc. Animal Production* (1921), 82–84.

[5] E. C. Sherrard and G. W. Blanco, *J. Ind. Eng. Chem.*, **13** (1921), 61.

ground barley, 30 parts wheat bran, and 15 parts linseed meal; or 60 parts yellow corn, 20 parts wheat bran, and 20 parts linseed meal. It was found that when 1 part of barley or corn was replaced with 2 parts of hydrolyzed wood, up to the point where the hydrolyzed wood formed one-fourth to one-third of the concentrate mixture, the cows not only maintained their milk and fat production, but showed a gain in weight over animals maintained on the regular ration.

More recent experiments[1] with dairy cows have shown that hydrolyzed wood, based on a comparison of the digestible nutrients, has a value from one-tenth to one-fourteenth that of corn meal; and on an energy basis, one-seventh to one-eighth. The large proportion of material of no nutritive value and the unpalatability of the hydrolyzed wood render its use inadvisable except under special circumstances.

The purification of sugars from wood so that they are suitable for human consumption has not been accomplished.[2]

Various attempts have been made to determine the food value of cellulose substances *in vitro.* Since the digestible portion of crude fiber consists entirely of cellulose,[3] Mach and Lederle[4] have proposed a method based on the solubility of the crude fiber in cuprammonium. Coniferous wood flour contains about 60 per cent of crude fiber, of which 34 to 38 per cent is soluble in cuprammonium. The method is considered unreliable by Lehmann,[5] owing to the high solubility of the crude fiber of so "hopeless" a foodstuff as wood.

The cæcal and colon fluids of the horse have also been employed.[6] With colon fluid, sulphite pulp and straw pulp were destroyed to the extent of 37.5 per cent, while raw spruce flour was unattacked. Another method[7] is based on the determination of the amount of lignin present in the material as measured by the weight of chlorine absorbed. Lignin protects the carbohydrates from digestion so that, in general, as the amount of lignin decreases, the digestibility increases. Substances, such as wood, taking up 45 per cent of chlorine, are indigestible; 30 per cent, moderately digestible; and 20 per cent or less, readily digestible. Natural straws have a chlorine number of 31.8.

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[1] T. E. Woodward *et al.*, *U. S. Dept. Agr.*, *Bull.*, **1272** (1924).

[2] A. Jonscher, *Z. öffentl. Chem.*, **24** (1918), 279; Lassar-Cohn, *Chem. Zentr.*, **II** (1918), 778.

[3] F. Honcamp and F. Ries, *Landw. Vers.-Sta.*, **84** (1914), 301.

[4] F. Mach and P. Lederle, *Landw. Vers.-Sta.*, **90** (1917), 269; **91** (1917), 137.

[5] Lehmann, *Landw. Vers.-Sta.*, **91** (1917), 154.

[6] P. Waentig and W. Gierisch, *Z. physiol. Chem.*, **107** (1919), 213–224.

[7] P. Waentig and W. Gierisch, *Z. physiol. Chem.*, **103** (1918), 87–103.

Some of the lower organisms, such as termites, utilize the wood into which they bore.[1] Cleveland,[2] in a very interesting research, found that of the four families of termites, *Kalotermitidœ, Rhinotermitidœ, Mastotermitidœ,* and *Termitidœ,* the first three were hosts to large numbers of intestinal protozoa. They were able to lead an active existence on a purely cellulose diet. When defaunated by incubation at 36° for 24 hours, at which point the protozoa were killed, the termites were unable to digest sound wood and died within 10 to 20 days; on humus and decayed wood, however, they were able to live indefinitely. Reinfection of the incubated termites with protozoa permitted them to utilize their normal food, thus showing clearly that digestion of wood was dependent on the presence of protozoa.

The various species of marine borers, *Teredo, Xylotrya,* and *Limnoria,* are extremely destructive to structural timbers. The prevailing opinion[3] has been that the borings are not digested. The recent work of Dore and Miller[4] shows that the teredo utilizes a considerable portion of the wood passing through its alimentary canal. The borings lost about 80 per cent of their cellulose and 15 to 56 per cent of their hemicelluloses. The ejected material contained uniformly 21 per cent of cellulose and 55 per cent of lignin, indicating that this ratio represents the limit of digestibility. Harington[5] has furnished inconclusive evidence that the liver of *Teredo norvegica* contains an enzyme producing glucose from sawdust. The opinion appears to prevail that digestion takes place in the direct presence of enzymes.[4]

[1] N. Banks and T. E. Snyder, *U. S. Nat. Museum, Bull.,* **108** (1920).

[2] L. R. Cleveland, *Biol. Bull. Marine Biol. Lab.,* **46** (1924), 178–223.

[3] C. A. Kofoid, *Proc. Am. Wood-Preservers' Assoc.,* (1921), 214–215.

[4] W. H. Dore and R. C. Miller, *Univ. Calif. Pub. in Zoology,* **22** (1923), 383–400.

[5] C. R. Harington, *Biochem. J.,* **15** (1921), 736–741; *J. Soc. Chem. Ind.,* **42** (1923), 1178A.

It will probably be found that the digestive tract of the teredo, like that of the higher animals, contains bacteria that decompose the carbohydrates to fatty acids. This view is supported by the observation of Harington[1] that the larvæ of the teredo are positively chemotropic to hydrochloric, acetic, and malic acids. He suggests that malic acid is the attractive substance in the wood.

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[1] C. R. Harington, *l. c.*

CHAPTER XVI

ANALYTICAL METHODS

Of all of the numerous methods which have been proposed for determining the various constituents and groupings in wood and allied substances, only the determination of methoxyl is beyond "suspicion." It is the purpose of this chapter to outline those methods which have proved most serviceable to date and to point out wherein they fail to measure up to the degree of precision desired for quantitative work.

Preparation of Sample.—In order to secure uniformity of procedure, it is suggested that all determinations be made on wood powder passing an 80-mesh but retained by a 100-mesh sieve. A representative sample of the wood is converted into sawdust. A disk saw provided with a guard so arranged as to cut just the width of the saw is a convenient means for converting a piece of wood almost completely into sawdust.[1] This is then ground in a disk mill and sifted, all material passing an 80-mesh sieve being set aside. The coarse material is then reground and sifted. After all the powder passes an 80-mesh sieve, it is again sifted, and that passing a 100-mesh sieve is rejected. The air-dry sample is preserved in a sealed jar so that the moisture content need be determined but once.

Determination of Water.—The sample weighing 3 to 4 grams is placed in a weighing bottle and dried in an oven at 105° until no decrease in weight takes place. This usually requires 4 to 6 hours. The weighing bottle should be closed while it is cooling in the desiccator. All chemical determinations should be made on the air-dry material and the results calculated to the dry weight. Drying of wood or pulp[2] at elevated temperatures may change the chemical constants.

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[1] A. W. Schorger, *J. Ind. Eng. Chem.*, **9** (1917), 556.

[2] E. Richter, *Wochbl. Papierfabr.*, **44** (1913), 1198.

Drying over phosphorus pentoxide, even with a vacuum, is tedious and, except under special conditions, unnecessary. It has been found that no appreciable error is introduced by drying in the oven.[1]

A rapid and fairly accurate method for determining moisture has been developed by Schwalbe.[2] The sample is placed in a copper retort, or a pyrex distilling flask, and covered with xylene. The outlet tube is bent downwards so that it may be inserted into a graduated funnel, cooled by running water. The vessel is then heated. The distillate separates into an upper layer of xylene, and a lower of water, whose volume is read.

Cold-water-soluble.—Two grams of wood powder, 80 to 100 mesh, are placed in a 400-cubic-centimeter beaker, 300 cubic centimeters of water added, and allowed to digest at room temperature with frequent stirring for 48 hours. The wood is then transferred to a tared alundum crucible, washed with cold water, dried, and weighed in a weighing bottle.

Hot-water-soluble.—Two grams of wood powder are digested with 100 cubic centimeters of water in a 300-cubic-centimeter Erlenmeyer flask provided with a reflux condenser. After boiling gently for 3 hours, the wood is transferred to a tared alundum crucible, washed with hot water, dried, and weighed. The loss in weight represents the portion soluble in hot water.

Alkali-soluble.—Two grams of the powder are placed in a 250-cubic-centimeter beaker and 100 cubic centimeters of a 1 per cent solution of sodium hydroxide added. The beaker is placed in a bath of boiling water, covered with a watch glass, and with occasional stirring, left for 1 hour. The wood is filtered off, washed with hot water, dilute acetic acid, and water, dried, and weighed.

Ether and Alcohol Extracts.—The extract varies with the nature of the solvent and the fineness of the sample. Unbleached sulphite pulp gave 0.58 per cent of resin on extraction with ether; after reduction to friable hydrocellulose by treatment with acid,

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[1] M. Renker, "Über Bestimmungsmethoden der Cellulose" (1910); F. Zweigler, *Papier-Fabr.*, **10** (1912), 1364; A. W. Schorger, *J. Ind. Eng. Chem.*, **9** (1917), 561.

[2] C. G. Schwalbe, *Z. angew. Chem.*, **21** (1908), 400.

1.09 per cent.[1] Little is known of the nature of the ether extract from hardwoods. The extract from coniferous woods contains fats and resin, of which abietic acid is the principal constituent. The alcohol extract contains tannins, linoxyn, highly oxidized resins, and resinous substances related to lignin. Under ordinary circumstances the amount of carbohydrates extracted is very slight. Sugars are present in most species in only very small amounts.

Steinschneider[2] found that the ether extract remained constant after 5 hours, while the alcohol extract increased up to 20 hours.

ETHER EXTRACT		ALCOHOL EXTRACT	
HOURS	PER CENT	HOURS	PER CENT
5	1.15	5	1.54
8	1.17	8	1.62
12	1.14	10	1.70
		16	1.79
		20	1.84
		24	1.82

The chemical constants for the two extracts were practically identical. Von Euler[3] recommends that the extraction with alcohol be continued for 24 hours, since complete extraction requires several days.

Procedure.—A sample of 3 to 4 grams of dry wood powder is extracted with ether in a Soxhlet extractor for 6 hours. The solvent is driven off and the residue in the extraction flask dried and weighed.

The ether is evaporated from the extraction thimble and the wood extracted for 8 hours with alcohol.

Ash.—Three to five grams of wood are incinerated in a platinum dish in an electric muffle furnace at a dull-red heat. The ash is stirred occasionally with a platinum wire to insure complete combustion.

Determination of Nitrogen.[4]—Place 3.5 grams of the substance in a Kjeldahl flask of 550-cubic-centimeter capacity, add 10 grams of pure anhydrous sodium sulphate, 0.3 gram of crystalline copper sulphate, and 25 grams of concentrated sulphuric acid. Place the flask in an inclined position and heat below the boiling point of the acid until frothing has ceased. Then increase the heat until the acid boils briskly and digest for a time after the mixture is colorless or nearly so, or until oxidation is complete.

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[1] C. G. SCHWALBE, *Z. angew. Chem.*, **32** (1919), 125.

[2] A. STEINSCHNEIDER, *Z. angew. Chem.*, **22** (1909), 1410; *cf.* E. OPFERMANN, *Ibid.*, 436.

[3] A. C. VON EULER, *Cellulosechemie*, **4** (1923), 4.

[4] "Methods of Analysis," A. O. A. C. (1919), p. 6.

After cooling, dilute with 200 cubic centimeters of water, add a few pieces of pumice stone, and then, with careful cooling, sufficient (60 cubic centimeters) of a saturated solution of sodium hydroxide to make the solution strongly alkaline. Pour the alkali down the side of the flask so that it does not mix at once with the acid. Connect the flask immediately with a Kjeldahl bulb attached to a condenser. The tip of the condenser is provided with an adapter in contact with the bottom of a vessel containing 50 cubic centimeters of $0.1N$ hydrochloric acid and 0.5 cubic centimeter of methyl-red indicator. Mix the contents of the Kjeldahl flask by agitation, then heat until 150 cubic centimeters have distilled over. Titrate the distillate with $0.1N$ sodium hydroxide and calculate the nitrogen.

A blank should be run, using 3.5 grams of cane sugar, and a correction applied if necessary.

The nitrogen multiplied by 6.25 gives the protein.

Determination of Cellulose.—Methods based on the use of sodium hydroxide[1] at 170 to 180°, sodium peroxide,[2] a mixture of nitric acid and potassium chlorate,[3] hydrogen peroxide and ammonia,[4] nitric acid and potassium permanganate,[5] nitric acid,[6] and some other oxidizing agents have been found[7] to be unreliable, owing to degradation of the cellulose. The use of caustic alkalis, bisulphites, and acids produces hydrolysis of the cellulose.

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[1] G. Lange, *Z. angew. Chem.*, **8** (1895), 561; F. Hoppe-Seyler, *Z. physiol. Chem.*, **13** (1889), 77.

[2] A. Duschetschkin, *J. Russ. Phys.-Chem. Soc.*, **36** (1904), 71.

[3] F. Schulze, *Chem. Zentr.*, **28** (1857), 321.

[4] J. König, *Ber.*, **40** (1907), 4195.

[5] S. Zeisel and M. J. Stritar, *Ber.*, **35** (1902), 1252.

[6] R. Dmochowski and B. Tollens, *J. Landw.*, **58** (1910), 1; V. Rao and B. Tollens, *Ibid.*, **61** (1913), 237.

[7] M. Renker, "Über Bestimmungsmethoden der Cellulose," Berlin (1910), 107 pp.

Klason[1] determines cellulose with a solution of sodium bisulphite and sulphurous acid. The solution is prepared by dissolving 80 grams of sodium bisulphite in 500 cubic centimeters of water, adding 200 cubic centimeters of *N* hydrochloric acid and making up to 1 liter. The wood and the solution are placed in a pressure bottle and heated at 100° for 4 days. The old liquor is replaced with fresh and the heating repeated in this manner until there is no further action. Pine shows a cellulose content of 54 per cent, which is not reduced by continued heating with fresh liquor. The method consumes much time.

Lignin can be removed by heating wood with phenol alone or in the presence of a small amount of mineral acid.[2] The yield of cellulose is appreciably lower than by the chlorine method. The cellulose in the following table was determined by heating the wood on the water bath for 1 hour with phenol containing 0.1 per cent of hydrochloric.

Wood	Phenol method		Chlorine method	
	Cellulose, per cent	Pentosan in cellulose, per cent	Cellulose, per cent	Pentosan in cellulose, per cent
Spruce...............	48.3	4.6	58.0	10.0
Beech...............	46.4	7.9	62.6	27.1

The best methods available are based on oxidation and substitution of the lignin with halogens. The most convenient procedure is that of Cross and Bevan, in which gaseous chlorine is employed. Comparable results are obtained with bromine water and ammonia,[3] and with a saturated aqueous solution of chlorine, but their use consumes much time. To avoid injuring the cellulose and to secure uniform action on the lignin, Sieber[4] recently revived the use of chlorine water. Another modification comprises treating the moist wood with a solution of chlorine in carbon tetrachloride.[1] The chlorinated products are removed in the usual way with a hot 2 per cent solution of sodium sulphite. The results are very concordant. Undue oxidation is avoided, since the cellulose has a copper number of only 0.8 to 0.9 compared with 3.14 to 3.23 for cellulose obtained with chlorine gas.

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[1] P. Klason, *Papier-Fabr.*, **22** (1924), 373; *cf.* P. Klason, *Chem. Ztg.*, **27** (1903), 585; E. Hägglund and E. Grenqvist, C. A., **18** (1924), 1568.

[2] L. Kalb and V. Schoeller, *Cellulosechemie*, **4** (1923), 37–40.

[3] H. Müller in Hofmann's "Ber. über die Entwichl. d. chem. Industrie," III (1877), 27.

[4] R. Sieber, *Zellstoff u. Papier*, **3** (1923), 27.

The method of chlorinating the wood influences the yield of cellulose. The procedure of Sieber and Walter,[2] in which the wood is chlorinated in a Gooch crucible, has been used extensively. Mahood[3] obtained less cellulose by this procedure than by chlorination in a beaker in a closed vessel.[4] This may be due to a higher chlorinating temperature or to a higher concentration of chlorine when a crucible is used. The action of the chlorine on the cotton filter was sufficient to cause a plus error of 0.29 per cent in the cellulose determination.

Sample No.	Species	Cellulose	
		Sieber and Walter's apparatus, per cent	Schorger's apparatus, per cent
1	Western larch	50.97	52.73
1	Western larch	50.82	52.24
2	Western larch	53.51	56.84
2	Western larch	53.23	56.72

The time of chlorination and the concentration of the chlorine should be regulated. When wood is chlorinated, then heated with sodium sulphite solution, the loss in weight, as shown below, is almost proportional to the concentration of the chlorine.[5]

White spruce		Yellow birch	
Chlorine bubbles per minute	Loss in weight, per cent	Chlorine bubbles per minute	Loss in weight, per cent
52–53	12.84	44–45	15.31
77–78	16.31	72–74	21.57
120–122	22.58	120–122	26.11

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[1] E. Heuser and H. Casseus, *Papier-Fabr. Fest u. Auslandsheft,* **20** (1922), 80–93.

[2] R. Sieber and L. E. Walter, *Papier-Fabr.,* **11** (1913), 1179–1183.

[3] S. A. Mahood, *J. Ind. Eng. Chem.,* **12** (1920), 874.

[4] A. W. Schorger, *J. Ind. Eng. Chem.,* **9** (1917), 561.

[5] A. W. Schorger, *l.c.; cf.* B. Rassow and A. Zschenderlein, *Z. angew. Chem.,* **34** (1921), 205.

Overchlorination results in the formation of oxycellulose and loss of cellulose. Ritter[1] has shown that the lignin is removed as rapidly by chlorinating for only 3 minutes as for longer periods. Chlorination appears to be largely a surface phenomenon so that the reaction soon slows down. The shorter period of chlorination also improves the yield of cellulose.

The physical condition of the sample is of great importance. There have been used: raspings;[2] raspings passing a 75- but not a 100-mesh sieve;[3] shavings 0.005 inch thick made with a cabinet-maker's scraper;[4] powder of unstated dimensions; and powder passing an 80- but not a 100-mesh sieve.[5] Mahood[6] found that the largest yield of cellulose was obtained from wood powder passing an 80- but retained by a 100-mesh sieve.

Species	Size of powder, mesh	Cellulose, per cent
Western larch (*Larix occidentalis*)	40–60	49.16
	60–80	50.54
	80–100	52.49
	100–120	51.03
Eucalyptus (*Eucalyptus globulus*)	40–60	56.18
	60–80	56.92
	80–100	59.69
	100–120	59.09

The ideal form of material for determining cellulose is the individual fiber, but this is difficult to obtain. Wood in the form of powder is much more reactive, due to cutting of the fibers and exposure of the interior of the cell.[7] If the interior wall of the cell is approximately pure cellulose, this would be continuously exposed to oxidation by the chlorine. Klason[1] has expressed a preference for fibrous material. Wood in the form of powder gave a lower yield of cellulose by the sulphite method. He assumes that there are two forms of cellulose in wood, one of which is more susceptible to hydrolysis. Pine wood contains 54 per cent of cellulose, of which 47 per cent is cellulose I (α-cellulose) and 7 per cent cellulose II (β-cellulose).

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[1] G. J. Ritter, *J. Ind. Eng. Chem.*, **9** (1924), 947; G. J. Ritter and L. C. Fleck, *Ibid.*, 147.

[2] A. L. Dean and G. E. Tower, *J. Am. Chem. Soc.*, **29** (1907), 1119; R. Sieber, *Zellstoff u. Papier*, **3** (1923), 27.

[3] R. Sieber and L. E. Walter, *Papier-Fabr.*, **11** (1913), 1179.

[4] A. W. Schorger, *l.c.*

[5] B. Johnsen and R. W. Hovey, *J. Soc. Chem. Ind.*, **37** (1918), 132T.

[6] S. A. Mahood, *l.c.*

[7] P. Waentig, *Zellstoff u. Papier*, **2** (1922), 152.

Quantities of wood powder exceeding a few grams are not uniformly penetrated by chlorine as the removal of the lignin progresses. In spite of the objections to wood powder on chemical and manipulative grounds, it appears advisable to use this form of material, as it facilitates standardization of procedure.

The wood should not be subjected to acids or alkalis before chlorination. Preliminary purification with hot dilute sodium hydroxide as recommended by Cross and Bevan lowers the yield of cellulose.[2] Heating the sample with glycerine-acetic acid, as recommended by Johnsen and Hovey,[3] serves no useful purpose since the pentosan content of the resulting cellulose is only slightly below that obtained by the Cross and Bevan method.

Procedure.—Two grams of wood (80 to 100 mesh) held in a tared alundum crucible are extracted in a Soxhlet extractor with alcohol-benzene mixture (32 parts of alcohol and 68 parts of benzene) for 6 hours, dried by suction, and washed with hot water. The moist sample is transferred to a 250-cubic-centimeter beaker by means of a pointed glass rod. Complete removal of the contents of the crucible is attained finally by holding the suction flask at an angle, and with the suction applied, washing the particles of wood adhering to the wall, into the lowest point in the crucible. The wood is uniformly distributed over the bottom of the beaker with a glass rod and the beaker placed in the chlorinating apparatus (Fig. 9), where it is cooled by running water. Chlorine washed with water is now introduced at the rate of 40 bubbles per minute. After 3 to 5 minutes' chlorination, the beaker is removed, sulphur dioxide water added to destroy excess chlorine, and the contents filtered.

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[1] P. Klason, *Papier-Fabr.*, **22** (1924), 375.

[2] M. Renker, *l.c.*, 44; A. W. Schorger, *l.c.*

[3] B. Johnsen and R. W. Hovey, *l.c.*, 133T.

The residue is washed with water, returned to the beaker, and 100 cubic centimeters of 2 per cent sodium sulphite solution added. The beaker is held in a boiling water bath for 30 minutes, the contents filtered, washed, and again chlorinated. This operation is repeated until the chlorinated material fails to give a pink color when the sodium sulphite solution is added. Coniferous wood requires four to five chlorinations, hardwoods two to three chlorinations.

The cellulose is finally bleached by adding 20 cubic centimeters of 0.1 per cent potassium permanganate solution, allowing to stand 10 minutes, and rendering colorless with sulphur dioxide water. It is then filtered, washed, returned to the beaker, 200 cubic centimeters of water added, and heated on the steam bath with occasional stirring for 2 hours. The cellulose is filtered, washed with hot water, alcohol, and ether, and dried in the oven at 105° for 2 hours. The crucible is placed in a stoppered weighing bottle while cooling in the desiccator. It is then weighed. The ash is determined by incinerating a portion of the cellulose in a platinum dish.

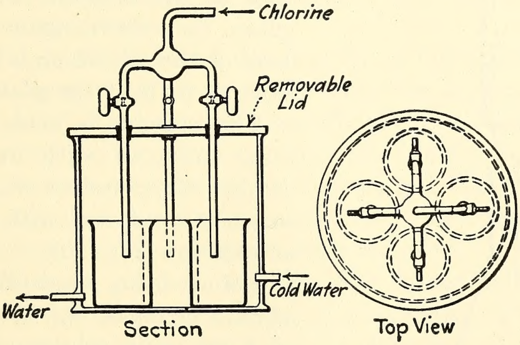

FIG. 9.—Apparatus for chlorinating wood. (*After Schorger.*)

The cellulose is boiled with water to remove traces of acids which are persistently retained. Removal of the potassium permanganate by the use of sulphurous acid results in the formation of manganese dithionate and sulphuric acid. If the cellulose is incompletely washed, as may happen if washing is performed in the crucible, it may darken during drying; furthermore, it will always contain variable quantities of carbohydrates soluble in hot water.[1] The formation of the water-soluble carbohydrates is not completely understood. Partial hydrolysis appears to take place during chlorination.

Procedure of Sieber and Walter.[2]—A filter plate is selected that fits closely into the bottom of a Gooch crucible. The plate is placed between two disks of fine muslin, the overlapping edges of which are sewn together. The plate is then inserted in the crucible and the muslin edges pressed down with a pointed spatula to obtain an effective seal. The needle is then passed through the bottom of the crucible, through the plate, then down again to form a loop of thread, which is tied at the bottom to hold the plate in place.

The crucible is held in a filter tube provided with an inverted rubber stopper over which fits an adapter connected with the source of chlorine (Fig. 10).

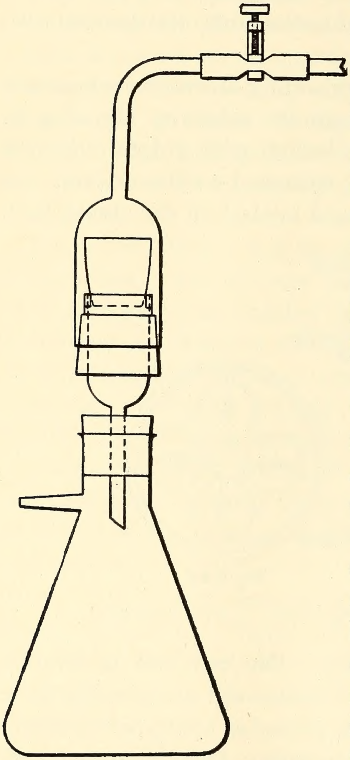

FIG. 10.—Apparatus for chlorinating wood. (*After Sieber and Dore.*)

Before being used, the crucible should be boiled for 15 minutes in a 3 per cent solution of sodium hydroxide, washed with hot water, dilute acetic acid, hot water, and finally boiled in water for 30 minutes to remove any impurities in the cotton. The crucible is then dried and weighed in a weighing bottle.

The crucible containing the sample is placed in the filter tube, which is inserted in a filter flask. Water is added to the sample and suction applied until the powder is porous. The wood should be pressed down uniformly and lightly with a glass rod to prevent channeling by the chlorine. The adapter is then put in place, suction applied, and washed chlorine gas drawn through the crucible for 5 minutes. The wood is then washed with sulphurous acid and water. The crucible is placed in a 50-cubic-centimeter beaker, which is filled with sodium sulphite to within a quarter of an inch of the top of the crucible, then heated in a boiling water bath for 45 minutes. The crucible is returned to the filter tube, the contents washed with water, and again chlorinated. This procedure is repeated until all the lignin is removed.

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[1] E. C. SHERRARD and G. W. BLANCO, *J. Ind. Eng. Chem.*, **15** (1923), 1166; G. J. RITTER, *Ibid.*, **16** (1924), 947.

[2] R. SIEBER and L. E. WALTER, *Papier-Fabr.*, **11** (1913), 1179.

The purification is carried out in the same way as by the Cross and Bevan method. All operations are performed without removing the sample from the crucible until the very end, when the bleached cellulose should be washed into a beaker for the final heating with water.

The cellulose obtained by chlorination is not pure. A small amount of lignin may be present. This can be determined in the usual way. The cellulose generally gives a slight methoxyl reaction, even though the usual tests for lignin fail.[1] Johnsen and Hovey[2] obtained 0.135 per cent of methyl, CH_3, though the cellulose gave no color reaction for lignin, and dissolved to a colorless solution in concentrated sulphuric acid.

In addition to normal cellulose, the crude cellulose may contain mannan, fructosan, xylan, and araban. The cellulose from coniferous woods contains mainly mannan and xylan, only a small amount of fructosan being present. The principal hemicellulose in hardwood cellulose is xylan. Mannan and pentosans may be estimated in the regular way. The normal cellulose present is best determined as α-cellulose. The determination of α-cellulose in cellulose that has been isolated by chlorination may not afford a true measure of the original α-cellulose in the wood unless the chlorination is carefully controlled.

The α-cellulose in sulphite pulp decreased but slightly as a result of chlorinating for 30 minutes, but dropped from 85 to 69 per cent after 4 hours' chlorination.[3] The loss resulted in an increase in β-cellulose.

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[1] A. W. Schorger, *l.c.*

[2] B. Johnsen and R. W. Hovey, *l.c.*, 134T.

[3] M. W. Bray and T. M. Andrews, *Paper Trade J.*, **76,** 8 (1923), 47.

Chlorine Dioxide Method.—A recent and promising method for determining cellulose involves the use of chlorine dioxide. Pine wood, free from resin, may be obtained free from lignin with 13.5 per cent of its weight of chlorine dioxide.[1] The lignin can be removed in one to two treatments in comparison with four to five by the chlorine method. Heuser and Merlau[2] have compared the two methods on spruce. The hexosans appear to remain intact in the cellulose skeleton, while a portion of the pentosans are removed during the treatment with sodium sulphite.

Method	Cellulose, per cent	Carbohydrates in cellulose		
		Pentosan, per cent	Mannan, per cent	Pure* cellulose, per cent
Chlorine dioxide......	62.71	4.44	5.43	52.84
Chlorine.............	59.24	4.90	2.09	52.28

*Determination of pure cellulose by difference is not strictly accurate.

Preparation of Chlorine Dioxide Solution.[2]—To a mixture of 240 grams of potassium chlorate and 200 grams of crystalline oxalic acid in a 1.5-liter round flask, is added a cold solution of 120 cubic centimeters of sulphuric acid in 400 cubic centimeters of water. The flask is then warmed in a water bath, the temperature being held at 50 to 60°. The gas evolved is washed with a small amount of water and absorbed in water in Woulff bottles surrounded by a cooling mixture. The reaction is complete in 8 to 9 hours. The carbon dioxide formed from the oxalic acid reduces the danger of explosion of the chlorine dioxide. The contents of the bottles are mixed and the amount of chlorine dioxide present is determined.

Titration of Chlorine Dioxide Solution.[3]—There are required (Fig. 11): a 100-cubic-centimeter burette having a ground-glass stopper and a long tip; and a 500-cubic-centimeter Erlenmeyer flask having a ground-glass stopper which is pierced by a filter tube of 50-cubic-centimeter capacity, and furnished with a stopcock. Fill the burette with the chlorine dioxide solution cooled to +7° and reverse 10 times to secure mixing. Relieve the pressure frequently by removal of the stopper. Run out a few cubic centimeters and read the meniscus. Insert the tip of the burette into the Erlenmeyer flask containing 100 cubic centimeters of water. Slowly run 10 cubic centimeters of the chlorine dioxide solution into the flask so that it forms a layer beneath the water. Insert the filter tube, close the cock, weight the flask with a lead ring, and place it in a cooling mixture to obtain a vacuum.

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[1] E. SCHMIDT *et al.*, *Ber.*, **54** (1921), 1860, 3241; **56** (1923), 23, 1438; **57** (1924), 1834.

[2] E. HEUSER and O. MERLAU, *Cellulosechemie*, **4** (1923), 101–109.

[3] E. SCHMIDT and E. GRAUMANN, *Ber.*, **54** (1921), 1862.

Introduce: (1) 1.5 cubic centimeters of $2N$ aqueous potassium iodide solution;[1] (2) 3 cubic centimeters of $2N$ sulphuric acid; (3) wash down with 2 to 3 cubic centimeters of water. Take care that no air enters the flask on introducing the solutions. Shake the flask vigorously and let stand 5 minutes at room temperature. Return to cooling mixture and add $0.2N$ sodium thiosulphate through the tube until most of the iodine is neutralized. Wash the tube with a little water. Shake the flask vigorously, cool, and relieve the pressure by drawing in a few cubic centimeters of water. Remove the tube, wash with a little water, and complete the titration, using starch as the indicator. The limit of error is ± 2 per cent.

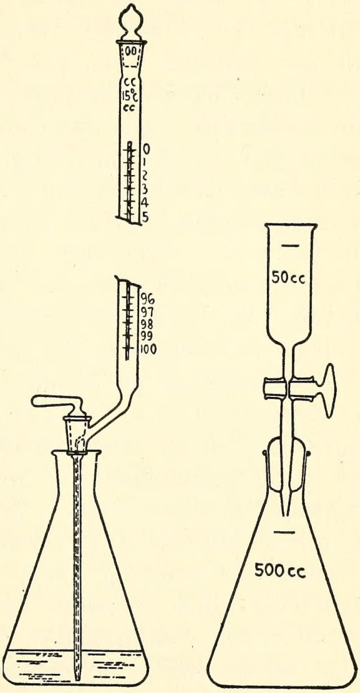

Fig. 11.—Apparatus for standardizing chlorine dioxide solutions. (*After Schmidt and Graumann.*)

1 cubic centimeter of $0.2N$ $Na_2S_2O_3$ = 0.0026984 gram of ClO_2.

Unless the reaction of the chlorine dioxide with the lignin is being studied quantitatively, all of the above precautions are not necessary, as moderate variations in the concentration of the chlorine dioxide do not appear to influence the yield of cellulose. Schmidt and Graumann used an 0.3 per cent solution and Heuser and Merlau[1] a 1.5 per cent solution.

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[1] This is sufficient for 10 cubic centimeters of $0.2N$ chlorine dioxide solution.

Procedure.[1]—In a glass-stoppered Erlenmeyer flask, place 0.5 gram of wood, previously exhausted with alcohol-benzene mixture, and 100 cubic centimeters of 1.5 per cent chlorine dioxide solution. Let stand in a cool place with frequent shaking. The wood acquires a red tinge. Filter after 48 hours and wash with warm water until the chlorine dioxide disappears, as shown by the inactivity of the filtrate towards acidified potassium iodide solution. Wash with hot 2 to 3 per cent sodium sulphite solution until the filtrate is colorless, then with warm water. One more treatment with chlorine dioxide is usually sufficient to remove all the lignin. Bleach the cellulose finally with 5 cubic centimeters of $0.2N$ (0.3 per cent) chlorine dioxide solution, wash, dry, and weigh.

Determination of Lignin.—Lignin even in its quantitative determination is the *bête noir* of wood chemistry. After careful consideration, the determination of lignin was originally omitted from the examination of woods[2] since no method available appeared to be accurate. This condition obtains today in spite of a large amount of intervening work. There is still no known method for isolating lignin unchanged. The most practical methods, which are based on the use of strong mineral acids, result in dehydration and hydrolysis of the lignin, and humification of the sugars on prolonged treatment. There is partial removal of the methoxyl groups, while the acetyl groups may be completely saponified. Deeper-seated changes likewise take place, since the isolated lignin is almost insoluble in bisulphite solutions[3] and is insoluble in sulphurous acid.[4]

The direct methods are usually adaptations of the use of mineral acids for complete hydrolysis of the carbohydrates in wood.

[1] E. Heuser and O. Merlau, *l.c.*, 105.

[2] A. W. Schorger, *J. Ind. Eng. Chem.*, **9** (1917), 556.

[3] E. Hägglund, *Arkiv Kemi, Mineral. Geol.*, **7**, 8 (1918), 1.

[4] F. König, *Cellulosechemie*, **2** (1921), 112.

Hydrochloric Acid Method.—Cellulose dissolves rapidly in hydrochloric acid of a concentration of 41 per cent and higher.[1] The wood is placed in a glass-stoppered flask, covered with 20 parts of hydrochloric acid (sp. gr. 1.205), and with frequent shaking let stand in a cool place. The following morning, if the wood is free from cellulose, the contents of the flask are diluted with 10 volumes of water, filtered, and washed until the filtrate no longer reacts with silver nitrate.

Fuming hydrochloric acid is exceedingly unpleasant to handle. Krull[2] avoids it by using hydrogen chloride gas. Five grams of wood moistened with 15 cubic centimeters of water are placed in a Claisen flask cooled with ice and saturated with hydrogen chloride gas produced by dropping concentrated sulphuric acid into concentrated hydrochloric acid. After standing 20 to 24 hours most of the hydrochloric acid is removed by a vacuum of 14 to 19 millimeters, the flask being gradually warmed to 70°. The dry residue contains 0.5 per cent hydrogen chloride. It is diluted to a definite volume and boiled for 8 hours under a reflux condenser.

The removal of the hydrochloric acid in determining lignin is unnecessary. The hydrolyzed wood is diluted with water until the concentration of the acid is about 3 per cent, boiled for 2 hours under a reflux condenser, and the lignin filtered off.

König and Becker[3] used 6 cubic centimeters of water to 1 gram of wood to secure greater fluidity. The water is advantageously replaced by ordinary concentrated hydrochloric acid, in which case cooling the absorption vessel with water is sufficient.[4]

Another method is based on the hydrolysis of the carbohydrates by heating the wood with a 1 per cent solution of hydrochloric acid at 6 atmospheres' pressure for 6 to 7 hours.[5]

Sulphuric Acid Method.—The strength of acid usually employed is 72 per cent. This reagent was used by Ost and

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[1] R. Willstätter and L. Zechmeister, *Ber.*, **46** (1913), 2401.

[2] H. Krull, Diss. Danzig (1916), 19.

[3] J. König and E. Becker, *Z. angew. Chem.*, **32** (1919), 155.

[4] W. H. Dore, *J. Ind. Eng. Chem.*, **12** (1920), 985.

[5] J. König and E. Rump, *Z. Unters. Nahr. Genussm.*, **28** (1914), 177.

Wilkening[1] for hydrolyzing cellulose, but it had been applied to the determination of lignin in 1868.[2]

Becker[3] determines lignin in pulp by mixing 1 gram with 20 cubic centimeters of 72 per cent sulphuric acid with a glass rod. When the mass becomes gelatinous, 80 cubic centimeters of acid are added and the mixture allowed to stand 24 hours. It is then diluted with 1.5 parts of water, filtered, washed with hot water, dried, weighed, ashed, and the ash deducted. Dilution and consequental precipitation of colloidal cellulose may be avoided by heating the acid mixture at 30 to 35°.[4] At this temperature the fluidity is sufficient to allow filtration without dilution.

Filtration of the lignin is greatly facilitated by diluting the mixture and boiling for several hours, whereby the colloidal carbohydrates present are hydrolyzed.[5] Mahood and Cable[6] treat 2 grams of wood with 10 parts by weight of 72 per cent acid, let stand 15 hours, dilute to an acid concentration of 3 per cent, and boil for 2 hours before filtering. The amount of acid used for hydrolysis should be increased to 15 cubic centimeters per gram.

Klason[7] treats 1 gram of wood with 50 cubic centimeters of 64 per cent sulphuric acid and, with stirring, lets stand overnight. The results are not affected by standing a further 24 hours. The mixture is diluted, filtered, and washed with cold or warm water. Resin and fats are removed by washing with 50 cubic centimeters of hot alcohol, then with 5 cubic centimeters of $0.1N$ potassium hydroxide to neutralize residual sulphuric acid. The lignin is then washed, dried, weighed, and ashed.

Whatever acid is used, a certain amount remains in the lignin. Lignin isolated with 72 per cent sulphuric acid contained 0.045 per cent sulphuric acid as SO_3.[8] König[9] could not obtain

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[1] H. Ost and L. Wilkening, *Chem. Ztg.*, **34** (1910), 461.

[2] E. Fremy and A. Terreil, *Bull. soc. chim.*, **9** (1868), 439.

[3] E. Becker, *Papier-Fabr.*, **17** (1919), 1325.

[4] R. Sieber and P. Rosenlund, *Zellstoff u. Papier*, **2** (1922), 251.

[5] J. König and E. Becker, *l.c.*

[6] S. A. Mahood and D. E. Cable, *J. Ind. Eng. Chem.*, **14** (1922), 933.

[7] P. Klason, *Cellulosechemie*, **4** (1923), 81–84; *Svensk Pappers-Tid.*, **26** (1923), 319.

[8] J. König and E. Rump, "Chemie und Struktur der Pflanzen-Zellmembran" (1914), p. 37.

[9] F. König, *Cellulosechemie*, **2** (1921), 112.

Willstätter lignin free from chlorine even by prolonged washing. Hägglund[1] found 1.63 per cent of chlorine in lignin isolated with fuming hydrochloric acid within 15 minutes, while Ungar[2] found 2.5 per cent after 25 hours' action. Waentig and Gierisch[3] obtained 1.95 per cent of chlorine. The presence in the lignin of variable amounts of furfural-producing substances has been discussed in the chapter on lignin.

Fuming hydrochloric acid and 72 per cent sulphuric acid give comparable results with coniferous wood. The results with sulphuric acid are less satisfactory with the hardwoods, owing to partial solution of the lignin.[4] Schwalbe and Becker,[5] on the other hand, thought that the lignin determination made on hemp sprits with sulphuric acid was too high, and that the actual lignin content was about 20 instead of 30 per cent as found. Regardless of the acid used, considerable variations in the lignin content of Norway spruce have been reported. Heuser and Skiöldebrand[6] obtained 33.12 per cent lignin by two treatments with 42 per cent hydrochloric acid; Hägglund,[7] 28 per cent after allowing 43 per cent hydrochloric acid to react for 15 minutes; Schwalbe and Becker,[8] 28.29 per cent by either the Willstätter or the Krull method, and 30 per cent with sulphuric acid.[9]

Mitscherlich pulp was found to contain 4.8 per cent of lignin by Becker's method. When the acid was diluted and boiled to remove colloidal carbohydrates, the amount of lignin was increased. Dilution to 10 volumes and boiling for 3 hours gave 6.00 per cent of lignin. Krull's method and that of König and Rump using 1 per cent hydrochloric acid gave too high results.[10]

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[1] E. Hägglund, *Arkiv Kemi, Mineral. Geol.*, **7,** 8 (1918), 1.

[2] E. Ungar, Diss. Zürich (1914), 63.

[3] P. Waentig and W. Gierisch, *Z. angew. Chem.*, **32** (1919), 173.

[4] J. König and E. Becker, *Z. angew. Chem.*, **32** (1919), 155; W. H. Dore, *J. Ind. Eng. Chem.*, **11** (1919), 562; **12** (1920), 984; B. Johnsen and R. W. Hovey, *J. Soc. Chem. Ind.*, **37** (1918), 137T.

[5] C. G. Schwalbe and E. Becker, *Z. angew. Chem.*, **32** (1919), 126.

[6] E. Heuser and C. Skiöldebrand, *Z. angew. Chem.*, **32** (1919), 41.

[7] E. Hägglund, *l.c.*

[8] C. G. Schwalbe and E. Becker, *Z. angew. Chem.*, **32** (1919), 229.

[9] C. G. Schwalbe and E. Becker, *Z. angew. Chem.*, **32** (1919), 128.

[10] E. Heuser and G. Wenzel, *Papier-Fabr.*, **19** (1921), 1177–1184.

Lignin dissolves on repeated treatment with acids.[1] Pine wood gave 22 to 26 per cent of lignin by the use of fuming hydrochloric acid. Alternate treatment of this lignin with cold, strong acid and boiling dilute acid caused more than half of the lignin to dissolve.

According to Dore,[2] a pure lignin is not obtained unless the wood is first extracted with alcohol-benzene mixture, water, and cold 5 per cent sodium hydroxide. The methoxyl content of live oak was not affected by the above complete purification, while the acetyl groups were almost completely eliminated. The completely purified wood contained 20.25 per cent of lignin (Krull's method) and that extracted only with alcohol and benzene, 22.11 to 25.53 per cent. It remains to be shown that the sodium hydroxide does not remove a portion of the lignin. Coniferous wood that had been extracted with alcohol and benzene was treated successively with water and hot 2 per cent sodium sulphite solution. After 13 such treatments the loss in weight was 23.4 per cent, represented by 5.2 per cent of lignin and 18.2 per cent of carbohydrates.[3]

According to von Euler,[4] preliminary extraction of the wood with alcohol removes some constituents related and properly belonging to the lignin. Results obtained by Becker's method should be increased 2 per cent for saponified acetyl groups, 3.53 per cent for alcohol-soluble resins, and decreased 5.7 per cent for sulphuric acid that cannot be removed from the lignin by washing. In fact, the errors balance so that the lignin content of spruce (30.5 per cent) as determined by Becker's method is approximately correct.

Treatment of wood with strong acids causes some loss of methoxyl. Spruce lignin, according to the methoxyl content of the wood, should contain 17.8 per cent of methoxyl. After 15 minutes' contact with 43 per cent hydrochloric acid, the methoxyl content dropped to 14.39 per cent.[5] Ungar[6] found 15.2

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[1] E. Hägglund and C. B. Björkman, *Biochem. Z.*, **147** (1924), 74–78.

[2] W. H. Dore, *J. Ind. Eng. Chem.*, **12** (1920), 986.

[3] A. C. von Euler, *Cellulosechemie*, **4** (1923), 109.

[4] A. C. von Euler, *Cellulosechemie*, **4** (1923), 1–11.

[5] E. Hägglund, *Arkiv Kemi, Mineral. Geol.*, **7**, 8 (1918), 1.

[6] E. Ungar, *l.c.*, 63.

per cent of methoxyl after the wood had been in contact with 41 per cent hydrochloric acid for 25 hours. According to Heuser and Wenzel,[1] spruce lignin as it occurs in wood contains 17.34 per cent of methoxyl. The loss of methoxyl with 43 per cent acid was:

	Loss of CH_3O, Per Cent
After 1 hour (17.34–14.69)	2.65
After 1.75 hours (17.34–14.45)	2.89
After three treatments of 18 hours each (17.34–11.98)	5.36

After 1.75 hours, the lignin had accordingly lost 16.6 per cent of its methoxyl.

The lignin content of various woods has been determined by König and Becker[2] by four methods: (1) heating with 1 per cent hydrochloric acid; (2) 72 per cent sulphuric acid; (3) fuming hydrochloric acid of sp. gr. 1.21; (4) Krull's method. The results for the conifers are fairly concordant by all methods. The hardwoods show the greatest variations, but this is not true for all of them. The agreement for aspen is excellent. With the exception of ash, the results are as concordant as could be

LIGNIN IN VARIOUS WOODS

No.	Wood	Lignin by			
		HCl 1 per cent, per cent	HCl gas, per cent	H_2SO_4 72 per cent, per cent	HCl sp. gr. 1.21, per cent
1	Fir	29.94	28.81	29.36	29.17
2	Fir	28.91	28.10	28.04	27.98
3	Pine	29.52	29.56	31.33	29.16
4	Birch	23.54	22.55	20.96	23.27
5	Birch	27.29	26.36	26.75	26.38
6	Aspen	22.14	22.36	22.06	22.45
7	Aspen	21.00	21.06	21.91	20.75
8	Beech	22.07	22.90	23.99	22.69
9	Ash	26.71	25.90	19.59	26.01
10	Willow	25.06	25.97	24.54	24.70
11	Alder	25.95	23.04	23.05	24.57

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[1] E. Heuser and G. Wenzel, *Papier-Fabr.*, **19** (1921), 1183.

[2] J. König and E. Becker, "Die Bestandteile des Holzes . . . ," Münster (1918), 47 pp.; *Z. angew. Chem.*, **32** (1919), 156.

expected and do not indicate a decided superiority of the fuming hydrochloric over the sulphuric acid method.

Many of the hardwoods contain in the cells and vessels deposits related to the tannins. They are largely insoluble in water and organic solvents, but soluble in alkalis. They are apparently much more soluble in sulphuric than in strong hydrochloric acid. The opinion is hazarded that the difference in results obtained with the two acids is due to these constituents, and for this reason the sulphuric acid method may be the more accurate of the two. Under present conditions all substances insoluble in the acids are estimated as lignin. In addition to extraction with alcohol-benzene mixture, there is needed a preliminary purification with a reagent that will not remove lignin. Dilute ammonia is promising for this purpose.

The sulphuric acid method is recommended for its convenience, in that it has not yet been shown to be less accurate than any of the other methods proposed.

Procedure.—Place an acid-treated, tared alundum crucible containing 2 grams of wood in a Soxhlet apparatus which is so filled with glass beads that the top of the crucible will project above the siphon. Extract the wood with alcohol-benzene mixture for 6 hours, dry by suction, wash thoroughly with hot water, and dry in the oven. Carefully transfer the wood with a brush to a 100-cubic-centimeter beaker, add 30 cubic centimeters of 72 per cent sulphuric acid, and mix thoroughly with a glass rod. Let stand in a desiccator with frequent stirring for 18 hours. If free from cellulose, transfer to a 1.5-liter beaker and dilute to 1200 cubic centimeters. Cover with a watch glass and boil gently for 2 hours. This volume is maintained, approximately, by the occasional addition of hot water. The lignin sometimes deposits on the glass and is troublesome to remove if a flask is used. Allow the contents of the beaker to cool and settle, siphon off the clear liquid, and filter off the lignin. Wash with cold or warm water until the filtrate is neutral; dry, and weigh. Transfer the lignin that can be easily removed to a tared platinum dish, incinerate, determine the percentage of ash, and apply the correction.

After standing in the acid 18 hours, a portion of the lignin should be tested for freedom from cellulose by: (1) examination under polarized light; (2) staining with iodine-sulphuric acid reagent; or (3) treatment with fresh acid for 6 hours, and testing of the neutralized filtrate with Fehling's solution. If there is no reduction, the removal of carbohydrates is complete.

Indirect methods, such as the calculation of lignin from the methoxyl content[1] of the sample, are valueless, since we do not know the true composition of lignin or the amount present in any particular species of wood. Furthermore, the methoxyl content of lignin varies between species, particularly between the two classes, conifers and hardwoods. The phloroglucinol absorption[2] method is empirical and subject to the same objections. It is useful, however, for determining the amount of mechanical pulp in mixtures.

A method for estimating lignin, based on the amount of chlorine absorbed, has been developed by Waentig and Gierisch.[3] Under specified conditions, pine wood took up 42.0 per cent of chlorine, calculated on the increase in weight. Pine wood by the Willstätter method contained 30.2 per cent of lignin, which was reduced to 28.7 per cent by extraction with alcohol and ether. This lignin on chlorination gave a chlorine value of 143.0. The calculated chlorine value ($42 \div 143 = 29.4$ per cent) is thus in good agreement with the direct determination.

Schmidt[4] assumed that the residue left from the alternate treatment of wood with chlorine dioxide and sodium sulphite, represented the carbohydrate skeleton, while the loss in weight was lignin. By this method, pine wood (*P. sylvestris*) showed 36.72 per cent, and beech 45.9 per cent of lignin. This assumption is erroneous, since considerable quantities of hemicelluloses are removed by treatment with hot sodium sulphite solution and washing with hot water.[5]

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[1] R. Benedict and M. Bamberger, *Chem. Ztg.*, **15** (1891), 221; T. von Fellenberg, *Biochem. Z.*, **85** (1918), 45.

[2] C. F. Cross, E. J. Bevan, and J. F. Briggs, *Chem. Ztg.*, **31** (1907), 725; T. Blasweiler, *Papier-Fabr.*, **18** (1920), 540; H. Krull and B. Mandelkow, *Ibid.*, **20** (1922), 1213.

[3] P. Waentig and W. Gierisch, *Z. angew. Chem.*, **32** (1919), 173–175.

[4] E. Schmidt *et al.*, *Ber.*, **54** (1921), 1860; **56** (1923), 23.

[5] E. Heuser and O. Merlau, *Cellulosechemie*, **4** (1923), 101–109; E. Heuser and A. Winsvold, *Ber.*, **56** (1923), 902; A. C. von Euler, *Cellulosechemie*, **4** (1923), 109–113.

Determination of Lignin in Pulps.—A rapid method for determining the degree of digestion of pulps is frequently useful.

Pure cellulose gives a colorless solution with sulphuric acid, while a pulp containing incrustants gives a colored one. A sample weighing 0.022 gram (0.020 gram dry) is placed in a 50-cubic-centimeter-glass-stoppered graduated tube, 20 cubic centimeters of concentrated sulphuric acid added, and the tube shaken until the pulp is dissolved. The color is compared with a similar solution of a pulp whose lignin content is known.[1] It is preferable to use an acid consisting of four parts of concentrated sulphuric acid and one part of water, since the stronger acid will soon produce a coloration with pure cellulose.[2]

Determination of Pectin.—The determination of pectin, by conversion of the pectinogen into pectin by means of sodium hydroxide and precipitating the resulting pectin as the calcium salt,[3] is of questionable value with wood. There is doubt as to the actual occurrence of pectin, especially in mature wood. Extraction with oxalic acid,[3] or ammonium oxalate, does not give a soluble pectin.[4] Von Fellenberg[5] found small quantities of pectin in wood by determining the amount of methyl alcohol formed under the conditions given below.

Procedure.—The raw material (1 to 2 grams) is freed from oils, fats, and resins by extraction with organic solvents. The substance is then placed in a 400-cubic-centimeter flask and 40 cubic centimeters of water added. The flask is heated and 20 cubic centimeters of water driven over to remove the last traces of volatile oil. To the hot (80 to 90°) residue, is added 5 cubic centimeters of 10 per cent sodium hydroxide (10 grams of NaOH in 90 cubic centimeters of water), the stoppers replaced, and the flask after thorough rotation allowed to stand 5 minutes. Now is added 2.5 cubic centimeters of sulphuric acid (1 volume of concentrated acid and 4 volumes of water) and 16.2 cubic centimeters distilled off. The receiver is a weighed test tube graduated for

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[1] P. Klason, *Papier-Fabr.*, **8** (1910), 1285–1286.

[2] G. von Zweigbergk, *Papier-Ztg.*, **37** (1912), 2506.

[3] R. G. W. Farnell, *Intern. Sugar J.*, **25** (1923), 248; S. B. Schryver and D. Haynes, *Biochem. J.*, **10** (1916), 539.

[4] A pectic substance has recently been isolated from beech wood by M. H. O'Dwyer, *Biochem. J.*, **19** (1925), 694.

[5] T. von Fellenberg, *Biochem. Z.*, **85** (1918), 68.

6, 10, and 16.2 cubic centimeters. The distillate is transferred to another flask, 5 drops of sodium hydroxide and 5 drops of 10 per cent silver nitrate solution added, and again distilled until 10 cubic centimeters is collected. By a final distillation, 6 cubic centimeters is collected. The weight of the distillate is found, and the amount of methyl alcohol present determined.

The following solutions are required:

1. Alcohol-sulphuric acid, prepared by dissolving 20 cubic centimeters of pure absolute ethyl alcohol or 21 cubic centimeters of 95 per cent alcohol in water, adding 40 cubic centimeters of concentrated sulphuric acid, cooling, and making up to 200 cubic centimeters.
2. Potassium permanganate solution, containing 5 grams of the salt in 100 cubic centimeters.
3. Oxalic acid solution, containing 8 grams of the acid in 100 cubic centimeters.
4. Pure concentrated sulphuric acid.
5. Fuchsine-sulphur dioxide solution,[1] prepared by dissolving 5 grams of fuchsine, 12 grams of sodium sulphite, and 100 cubic centimeters of *N* sulphuric acid in water and making up to 1 liter.
6. Methyl alcohol solution, containing 1 gram in 100 cubic centimeters, obtained by diluting 12.67 cubic centimeters (10 grams) of Kahlbaum's methyl alcohol to 1 liter; and another solution containing 0.1 gram in 100 cubic centimeters, obtained by dilution of a portion of the above with 9 volumes of water.

Determination of Methyl Alcohol.—Place 3 cubic centimeters of the methyl alcohol distillate in a wide test tube holding 40 to 50 cubic centimeters, add 1 cubic centimeter of the potassium permanganate solution, shake once, and let stand exactly 2 minutes. In the same way, prepare three standard solutions: the first containing 0.5 cubic centimeter of 1 per cent methyl alcohol (= 5 milligrams) and 2.5 cubic centimeters of water; the second, 1 cubic centimeter of 0.1 per cent solution (= 1 milligram) and 2 cubic centimeters of water; and the third, 0.3 cubic centimeter of 0.1 per cent solution (= 0.3 milligram) and 2.7 cubic centimeters of water. After 2 minutes, add to each solution 1 cubic centimeter of oxalic acid solution, inclining the test tube in such a way that the liquid carries with it any drops of $KMnO_4$ solution adhering to the wall of the tube. Now add 1 cubic centimeter of concentrated sulphuric with a pipette having a narrow tip, and immediately afterwards 5 cubic centimeters of the fuchsine solution. Mix so that the walls of the vessel are washed by the liquid. Let stand 1 hour and compare by eye the solution under examination with the standards. The exact comparison is made with the standard having the nearest depth of color. If the standard is 5 milligrams, dilute with 100 cubic centimeters of water; if one of the other two, dilute with 25 cubic centimeters of water and compare the colors in a sensitive colorimeter.

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[1] This solution must be carefully kept from light, preferably in a glass-stoppered bottle covered with black paper. So preserved, a solution deteriorated only 12 per cent in 6.5 months.

If the amount of methyl alcohol is considerably higher than that of the standard, repeat the color reaction, using an amount of the distillate that will correspond with the standard. The volume of distillate taken is made up to 3 cubic centimeters with water. For accurate determinations, the repetition is indispensable, since the highest accuracy is attainable only when the unknown agrees as closely as possible with the standard.

The methyl alcohol is calculated as follows:

$$M = \frac{g \cdot D}{10 \cdot d \cdot G}$$

G = sample in grams.
D = weight of distillate in grams.
d = cubic centimeters of distillate used in the reaction.
g = methyl alcohol found, in milligrams.

Example.—Sample used = 2 grams (G)
Weight of distillate = 6.49 grams (D)
Used for the reaction = 3.00 cubic centimeters (d)
Methyl alcohol in (d) = 1.20 milligrams (g)

$$M = \frac{1.20 \times 6.49}{10 \times 3 \times 2} = 0.13 \text{ per cent.}$$

Since there is 10 per cent of methyl alcohol in pectin,[1] the pectin content is obtained by multiplying the above by 10, making 1.30 per cent.

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[1] This statement requires confirmation.

A more promising method for estimating pectin is based on determining the carbon dioxide which is evolved when the galacturonic acid groups in pectin are decomposed by heating with hydrochloric acid.[1]

Determination of Methoxyl, CH_3O.—The principle of the methoxyl determination depends upon the formation of methyl iodide when the substance is heated with hydriodic acid. The methyl iodide is swept from the reaction flask by a current of carbon dioxide into absorption vessels containing an alcoholic 0.1*N* solution of silver nitrate, the methyl iodide being decomposed with the formation of silver iodide. When only a few determinations are being made, it is preferable to weigh the silver iodide directly.

The silver nitrate solution is prepared by dissolving 17 grams of the salt in 50 cubic centimeters of distilled water and making up to a liter with pure absolute alcohol. The silver nitrate and potassium sulphocyanate solutions are standardized as follows: A known weight (0.5 gram) of pure dry sodium chloride is made up to 250 cubic centimeters with distilled water; to 25-cubic-centimeter portions of the salt solution, known volumes (about 15 cubic centimeters) of the alcoholic silver nitrate solution are slowly added with constant stirring. The beakers are placed on a steam bath and heated until all the alcohol is expelled. A few drops of nitric acid are added, the precipitated silver chloride is filtered off, washed, and the filtrate titrated with the solution of potassium sulphocyanate. Use 5 cubic centimeters of a saturated solution of ferric alum acidified with nitric acid as the indicator. From the weight of sodium chloride employed, the strength of the silver nitrate and potassium sulphocyanate solutions can be readily calculated.

Procedure.—Twenty-five cubic centimeters of the silver nitrate solution is placed in the absorption bulb. To the heating flask containing 0.30 to 0.35 gram of wood powder, is added 15 cubic centimeters of hydriodic acid (sp. gr. 1.70). As soon as all the connections are made, the flask is heated in a glycerine bath held at 130°, and a stream of washed carbon dioxide is passed through the apparatus at the rate of 45 to 50 bubbles per minute. The heating is continued until the silver nitrate solution, at first milky, has become perfectly clear; this requires about 2 hours. The contents of the absorption bulb are washed into a beaker, made up to 300 cubic centimeters, and heated on the steam bath until the contents have evaporated to 50 cubic centimeters. A little nitric acid is added, the silver iodide filtered off, washed with hot water containing a little nitric acid, and the silver nitrate in the filtrate titrated with the potassium sulphocyanate solution.

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[1] D. R. Nanji *et. al.*, *J. Soc. Chem. Ind.*, **44** (1925), 253–258T; W. H. Dore, *J. Am. Chem. Soc.*, **48** (1926), 232–236.

1 cubic centimeter of $0.1N$ $AgNO_3$ = 0.0031 gram CH_3O.

Determination of Acetyl Groups in Wood.[1]—Two grams of wood powder is placed in a 250-cubic-centimeter Erlenmeyer flask and 100 cubic centimeters of 2.5 per cent sulphuric acid solution added. The flask is connected with a reflux condenser. The contents are boiled gently for 3 hours and allowed to cool. The interior of the condenser is washed down with a little distilled water and the contents of the flask are transferred to a 250-cubic-centimeter graduated flask. Distilled water free from carbon dioxide is added up to the mark, the solution allowed to stand several hours with frequent shaking, and then filtered.

A wide-mouthed, round-bottomed, 750-cubic-centimeter flask is provided with a rubber stopper containing: (1) a dropping funnel; (2) a glass tube drawn out to a capillary, closed with a rubber tube and pinchcock, and extending to the bottom of the flask; and (3) a Soxhlet connecting bulb tube. An ordinary condenser is used, to the end of which is attached for a receiver a 500-cubic-centimeter distilling flask cooled with a stream of water and connected with a manometer and suction pump.

A few pieces of pumice are placed in the boiling flask, to which is added 200 cubic centimeters of the filtrate obtained above (in the case of hardwoods use 100 cubic centimeters). The flask is heated in an oil bath maintained at 85°, while the pressure is reduced to 40 to 50 millimeters. When the contents of the flask reach about 20 cubic centimeters, distilled water free from carbon dioxide is added through the dropping funnel, drop by drop, at the same rate that distillation takes place. When 100 cubic centimeters of wash water have been distilled over, the distillate is titrated with $0.05N$ sodium hydroxide, using phenolphthalein as the indicator. If (*a*) 200 cubic centimeters or (*b*) 100 cubic centimeters of solution is taken for distillation, the number of cubic centimeters of sodium hydroxide used is multiplied by (*a*) 5/4 or (*b*) 5/2, respectively, and calculated as acetic acid.

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[1] A. W. SCHORGER, *J. Ind. Eng. Chem.*, **9** (1917), 559.

1 cubic centimeter of $0.05N$ NaOH = 0.0030 gram $CH_3.COOH$.

The acetic acid contains some formic acid. This may be determined, and the correction applied, by adding an excess of a saturated solution of mercuric chloride to the neutralized, concentrated distillate and heating on the water bath for 2 hours. The mercurous chloride formed by reduction is filtered off in a Gooch crucible, washed, dried at 100°, and weighed. The weight of mercurous chloride multiplied by 0.0975 gives the weight of formic acid.

Determination of Acetyl Groups in Cellulose Acetate.—Ost[1] treats 1 gram of cellulose acetate with 10 cubic centimeters of sulphuric acid (50 per cent by volume) with frequent shaking for 24 hours, whereby solution takes place. The solution is then diluted to 100 to 120 cubic centimeters with water and distilled with steam at a rate such that 500 to 600 cubic centimeters of distillate are collected in 1 hour. All the acetic acid is carried over in 3 to 4 hours. The distillate is then titrated with standard alkali. Hess[2] has modified this method by distilling off the acetic acid in a vacuum in the presence of steam.

Alkaline saponification is preferable, since acid hydrolysis gives rise to volatile acids due to the action of the sulphuric acid on the cellulose. Barnett[3] determines the acetyl groups in acetone-soluble cellulose acetates by dissolving the sample in acetone, adding an excess of standard sodium hydroxide, shaking in a stoppered flask, and letting stand a day. The excess alkali is then determined by titration with standard acid. Blanks are run on the original cellulose and the acetone, and the correction applied. The data on a cellulose diacetate were:

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[1] H. Ost and T. Katayama, *Z. angew. Chem.*, **25** (1912), 1469.

[2] K. Hess, *Ann.*, **435** (1924), 64.

[3] W. L. Barnett, *J. Soc. Chem. Ind.*, **40** (1921), 9T.

Substance	Weight, grams	Acetone, cubic centimeters	$0.1N$ NaOH, cubic centimeters	$0.1N$ H_2SO_4, cubic centimeters	Acetic acid, per cent
Cellulose acetate........	0.3167	30	47.0	18.85	48.98
Cellulose...............	0.3000	30	47.0	44.20	
Blank..................	......	30	47.0	45.90	

The loss due to the 0.3 gram of cellulose is 1.7 cubic centimeters of $0.1N$ sodium hydroxide. The titration figure for the cellulose acetate indicates a diacetate, so that approximately two-thirds of the ester is cellulose. Hence the number of cubic centimeters of alkali neutralized by the regenerated cellulose is

$$\frac{2}{3} \times \frac{0.3167}{0.30} \times 1.7 = 1.2 \text{ cubic centimeters.}$$

The alkali equivalent to the acetic acid is $45.9 - 18.85 - 1.2 = 25.85$ cubic centimeters, which represents 48.98 per cent acetic acid.

Knoevenagel and König[1] swell the cellulose acetate by warming with 75 per cent ethyl alcohol, and cool before adding the standard sodium hydroxide solution.

Determination of Pentosans.—The only pentosans that have been found in wood are xylan and araban. Their estimation is based on the formation of furfural and its quantitative determination. The results are usually calculated to "pentosan" by Kröber's tables, which means a value between xylan and araban. The determination is complicated by the formation of a small amount of furfural (less than 1 per cent) from hexoses and the uncertainty that all the remaining furfural is derived from pentosans. Glucuronic acid and oxycellulose yield furfural, but these substances are not definitely known to occur in wood.

There are additional complications. The usual procedure consists in distilling the raw material with 12 per cent hydrochloric acid and precipitating the furfural with phloroglucinol. The distillate contains varying amounts of substances which precipitate with the furfural phloroglucide. Fraps[2] found that a hydrochloric acid solution of furfural showed practically no loss of furfural on redistillation while distillates from plant substances showed apparent losses as high as 22.5 per cent.

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[1] E. Knoevenagel and K. König, *Cellulosechemie*, **3** (1922), 113.

[2] G. S. Fraps, *Am. Chem. J.*, **25** (1901), 501–508; *cf.* R. Jäger and E. Ungar, *Ber.*, **35** (1902), 4440.

Distillate from	Loss, Per Cent
Oak sawdust	6.9
Oxycellulose (by means of chromic acid)	13.8

The substances lost were termed furaloids. The furaloid substances could be destroyed by boiling 10 grams of the raw material with 1 liter of 1.25 per cent sulphuric acid for 30 minutes. This procedure may, however, lead to loss of pentoses. Since hexosans give some hydroxymethylfurfural the loss on redistillation may be partially due to destruction of this aldehyde;[1] as the furfural distillation is usually conducted, the formation of hydroxymethylfurfural is not of great importance.

The use of phloroglucinol for determining furfural was suggested by Councler.[2] The furfural phloroglucide precipitate has a variable composition,[3] except possibly under the most exact conditions. Jäger and Ungar[4] found 60.45 to 64.28 per cent of carbon in the crude phloroglucide precipitates from various plant substances. The condensation of phloroglucinol with pure furfural in the cold takes place mainly as follows:

$$C_6H_6O_3 + C_5H_4O_2 = C_{11}H_8O_4 + H_2O$$

Kröber[5] assumed that two molecules of water were eliminated. Goodwin and Tollens[6] found that one molecule of water was eliminated at room temperature and three at 80°, so that the precipitate had the composition $C_{11}H_4O_2$. For this reason, following the suggestion[7] to heat the distillate to 80 to 85°, cool and filter, instead of allowing it to stand overnight, would render it impossible[1] to use Kröber's tables.

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[1] M. Cunningham and C. Dorée, *Biochem. J.*, **8** (1914), 438.

[2] C. Councler, *Chem. Ztg.*, **18** (1894), 966.

[3] C. Councler, *Chem. Ztg.*, **18** (1894), 1617; B. Welbel and S. Zeisel, *Monatsh.*, **16** (1895), 310; E. Lázár, *Ibid.*, **34** (1913), 1941; E. Votocek and R. Potmesil, *Ber.*, **49** (1916), 1185.

[4] R. Jäger and E. Ungar, *Ber.*, **35** (1902), 4440.

[5] E. Kröber, *J. Landw.*, **48** (1900), 357.

[6] W. Goodwin and B. Tollens, *Ber.*, **37** (1904), 315.

[7] K. H. Böddener and B. Tollens, *J. Landw.*, **58** (1910), 232.

Distillation of pentoses with 12 per cent hydrochloric acid, as ordinarily conducted, gives only about 75 per cent of the theoretical yield of furfural. This may be rendered nearly quantitative by passing a current of steam through the flask while the contents are being distilled.[2] In order to use Kröber's tables, it is necessary to distill by the standard method, as otherwise the pentosan content would be too high.

Numerous methods for determining furfural which do not involve the use of phloroglucinol have been proposed, but have not been generally adopted.[3] The more recent methods are based on the oxidation of furfural with bromine. Van Eck[4] used an excess of bromine, a procedure by which Pervier and Gortner[5] could not obtain satisfactory results. These authors used just enough bromine to perform the oxidation and determined the end point electrometrically. The method is somewhat tedious. Powell and Whitaker[6] obtained good results by using an excess of bromine, whereby four atoms of bromine are consumed per molecule of furfural. The bromine method has the disadvantage that no correction can be applied for hydroxymethylfurfural, methylfurfural (if present), and oxidizable impurities that may be obtained in appreciable quantities from raw plant substances; however, the results obtained for wood pulp and purified wood by the bromine and phloroglucinol methods showed good agreement.

Phloroglucinol Method.—This method is purely empirical and all conditions, such as concentration of acid and rate of distillation, must be carefully observed; however, results can be duplicated closely.

The phloroglucinol solution is prepared by heating 11 grams of phloroglucinol in a beaker with 300 cubic centimeters of 12 per cent hydrochloric acid. When solution has taken place, dilute to 1500 cubic centimeters with 12 per cent hydrochloric acid. Before using, allow the solution to stand a week in order that diresorcin which vitiates the determination may crystallize out.

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[1] J. L. Wichers and B. Tollens, *J. Landw.*, **58** (1911), 238; C. G. Schwalbe, *Z. angew. Chem.*, **32** (1919), 229.

[2] A. Jolles, *Ber.*, **39** (1905), 96; *Z. anal. Chem.*, **45** (1906), 196; N. C. Pervier and R. A. Gortner, *J. Ind. Eng. Chem.*, **15** (1923), 1167, 1255.

[3] For a good review and bibliography see N. C. Pervier and R. A. Gortner, *l.c.*

[4] P. N. van Eck, C. A., **14** (1920), 509.

[5] N. C. Pervier and R. A. Gortner, *l.c.*

[6] W. J. Powell and H. Whittaker, *J. Soc. Chem. Ind.*, **43** (1924), 35T.

The aniline reagent is prepared by adding acetic acid or hydrochloric acid drop by drop to a mixture of equal volumes of aniline and water until a clear solution is obtained. Acetic acid may contain impurities that give a coloration with aniline. If the aniline reagent colors filter paper, as frequently happens with age, it should be rejected.

Place 1 to 2 grams of the sample (2 grams of coniferous wood or 1 gram of hardwood) in a 250-cubic-centimeter flask provided with a separatory funnel and an outlet tube, the connection with the flask being of ground glass. Attach the outlet tube to a condenser. Add 100 cubic centimeters of 12 per cent hydrochloric acid (sp. gr. 1.06) and distill at the rate of 30 cubic centimeters in 10 minutes. Pass the distillate through a small filter before entering the receiver. As soon as 30 cubic centimeters of distillate are collected, add 30 cubic centimeters of hydrochloric acid to the flask, and continue the distillation in this manner until the distillate is free from furfural. All of the furfural is usually obtained in the first 270 cubic centimeters of distillate. As long as furfural is formed, the distillate will give a pink color when a drop is allowed to merge with a drop of the aniline reagent on filter paper. Add 40 cubic centimeters of filtered phloroglucinol solution to the distillate, and make up to 400 cubic centimeters with hydrochloric acid. The solution soon turns greenish black and furfural phloroglucide precipitates. After standing 16 hours, test the supernatant liquid with the aniline reagent. If a pink color is obtained, it is necessary to add more phloroglucinol. This rarely happens with the quantities specified.

Filter off the furfural phloroglucide, using a tared Gooch crucible with a thick asbestos mat, taking care that the crucible is always partially filled with liquid. Wash with exactly 150 cubic centimeters of water, dry in an oven at 100 to 105° for 4 hours, transfer to a weighing bottle, cool in a desiccator and weigh. The precipitate is hygroscopic.

The crucible is placed in a narrow beaker and 20 cubic centimeters of 95 per cent alcohol added. The beaker is then placed for 10 minutes in a water bath maintained at 60°. The alcohol is removed with a suction pump and the process repeated (usually four or five times) until the alcohol that runs through is practically colorless. Pure furfural phloroglucide is not entirely insoluble in alcohol. Each extraction removes about 0.0014 gram.[1] The crucible is again weighed and the furfural phloroglucide calculated to furfural or pentosan by Kröber's tables or formulæ. The soluble phloroglucides are usually calculated to methylpentosan. In most cases this determination is meaningless, as it is based on impurities. It should be eliminated in the case of wood.

Furfural, pentose, or pentosan is calculated from the weight, *a*, of furfural phloroglucide. In the formulæ given below, the factor 0.0052 represents the amount of phloroglucide remaining dissolved in the hydrochloric acid. For a weight of phloroglucide

Under 0.03 gram:
  Furfural $= (a + 0.0052) \times 0.5170.$
  Pentoses $= (a + 0.0052) \times 1.0170.$
  Pentosans $= (a + 0.0052) \times 0.8949.$
Between 0.03 and 0.30 gram:
  Furfural $= (a + 0.0052) \times 0.5185.$
  Pentoses $= (a + 0.0052) \times 1.0075.$
  Pentosans $= (a + 0.0052) \times 0.8866.$
Over 0.30 gram:
  Furfural $= (a + 0.0052) \times 0.5180.$
  Pentoses $= (a + 0.0052) \times 1.0026.$
  Pentosans $= (a + 0.0052) \times 0.8824.$

Bromine Method.[2]—From 0.5 to 0.8 gram of material is distilled with 12 per cent hydrochloric acid until the distillate gives no further coloration with aniline hydrochloride. The distillate is then made up to 500 cubic centimeters with 12 per cent hydrochloric acid. Into each of four well-stoppered bottles, is pipetted 25 cubic centimeters of 0.1*N* sodium-bromide-bromate solution. To two of these bottles, is now added 200 cubic centimeters of the distillate and to the other two bottles 200 cubic centimeters of 12 per cent hydrochloric acid. The bottles are allowed to stand in the dark for 1 hour, and after the addition of 10 cubic centimeters of 10 per cent potassium iodide solution the liberated iodine is determined by titration with $0.1N$ sodium thiosulphate. The number of cubic centimeters required by the sample is subtracted from the number of cubic centimeters required by the blank, the difference being a measure of the furfural present. One cubic centimeter of $0.1N$ sodium thiosulphate is equivalent to 0.0024 gram of furfural.

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[1] W. B. Ellett and B. Tollens, *J. Landw.*, **53** (1905), 20.
[2] W. J. Powell and H. Whittaker, *J. Soc. Chem. Ind.*, **43** (1924), 36T.

Determination of Mannan.[1]—Place 10 grams of the finely ground sample, and 150 cubic centimeters of 5 per cent hydrochloric acid, in a 300-cubic-centimeter Erlenmeyer flask and boil gently under a reflux condenser for 3.5 hours. Filter with suction and wash the residue by the gradual addition of boiling water until 500 cubic centimeters of filtrate are collected. Cool the filtrate, neutralize with sodium carbonate, then make slightly acid with acetic acid. Concentrate the solution to 150 cubic centimeters, transfer to a 300-cubic-centimeter Erlenmeyer flask, add a mixture of 10 cubic centimeters of phenylhydrazine, 20 cubic centimeters of glacial acetic acid, and 20 cubic centimeters of water, and shake. If a bulky crystalline deposit forms at once, due to salting out of phenylhydrazine acetate, add sufficient water to cause it to dissolve. Filter rapidly through a wet filter paper to remove tarry impurities which may separate, wash the filter with a little water, and allow the filtrate to stand at room temperature with frequent shaking for 2 hours. Collect the precipitate of mannose phenylhydrazone in a tared Gooch crucible, wash with water to remove sodium chloride, then with acetone to remove resinous impurities, and finally with water to remove the last traces of salts. Dry and weigh the crucible.

The weight of the mannose phenylhydrazone multiplied by 0.6 gives mannan. When purified by recrystallization from 75 per cent alcohol, mannose phenylhydrazone forms colorless prisms melting at about 190°.

The method based on extracting the mannan with sodium hydroxide[2] and subsequently hydrolyzing it, gives low results due to incomplete extraction of the mannan.[3]

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[1] A. W. Schorger, *J. Ind. Eng. Chem.*, **9** (1917), 748.

[2] F. Lenze, B. Pleus, and J. Müller, *J. prakt. Chem.*, **101** (1920), 236.

[3] E. Heuser and W. Dammel, *Cellulosechemie*, **5** (1924), 45.

Determination of Galactan.—The determination of galactan in wood and other plant substances is only approximately correct. The estimation is based on oxidation to the difficultly soluble mucic acid. The oxidation of pure galactose is not quantitative and becomes erratic in the presence of much foreign organic matter. Failure to obtain theoretical yields is probably due to the formation of galacturonic acid which, like glucuronic acid, decomposes with the liberation of carbon dioxide.

Van der Haar,[1] who studied the determination of free and combined galactose, recommended that polysaccharides be hydrolyzed with sulphuric acid before oxidizing. This method had been tried with galactan and no benefit obtained.[2] The galactan in wood appears to be largely soluble in boiling water, but the last traces are difficult to remove from the associated water-insoluble colloids, unless the wood is very finely ground.

In the official method,[3] the sample is oxidized directly with nitric acid and the mucic acid formed is extracted from the insoluble plant residue with ammonium carbonate. Miyake[4] avoids alkaline extraction by diluting the concentrate with hot water, filtering, and evaporating until the mucic acid crystallizes. This method was used by Dore[5] on wood, but the amount of mucic acid obtained from the sample (5 grams) was too small for actual identification.

The determination of galactan by the direct oxidation of wood is uncertain. Large amounts of oxalic acid are formed from the lignin and hemicelluloses. Small amounts of galactan may escape detection, while if much is present, mucic acid may be deposited in the wood. The writer has had the best success by the method given below. The nitric acid is of such a strength that it has a hydrolyzing and but little oxidizing action during the preliminary extraction.

Procedure.—Extract 10 grams of wood powder with alcohol-benzene mixture. Transfer it to a 250-cubic-centimeter flask, add 150 cubic centimeters of 3 per cent nitric acid, and attach the flask to a reflux condenser. Heat the flask in a water bath for 2 hours. Filter on a Büchner funnel and wash with 250 cubic centimeters of boiling water. Transfer the filtrate to a porcelain dish, concentrate to 100 cubic centimeters, cool, and filter. Evaporate the filtrate to 10 cubic centimeters and transfer it to a 100-cubic-centimeter beaker, using 50 cubic centimeters of 25 per cent nitric acid (sp. gr. 1.115). Suspend the beaker in a water bath maintained at a temperature of 85 to 87°, and evaporate to 20 cubic centimeters. Let stand 24 hours. If no mucic acid has separated, concentrate to 5 to 10 cubic centimeters at a low temperature, and let stand 2 or 3 days. Add with stirring sufficient water to dissolve any oxalic acid that may have separated. Let stand 2 or 3 days, filter on a Gooch crucible, wash, dry, and weigh. Mucic acid forms a white, crystalline powder or crust, and melts at 212 to 215°. The weight of mucic acid multiplied by the factor 1.12 gives galactan.

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[1] A. W. van der Haar, *Chem. Weekblad,* **13** (1916), 498.

[2] A. W. Schorger and D. F. Smith, *J. Ind. Eng. Chem.,* **8** (1916), 498.

[3] "Methods of Analysis," A. O. A. C. (1920), 97.

[4] K. Miyake, *J. Coll. Agr., Tohoku. Imp. Univ.,* **4** (1912), 337.

[5] W. H. Dore, *J. Ind. Eng. Chem.,* **12** (1920), 476.

It is well to check the result by oxidation of a water extract of the wood. Boil 50 grams of wood powder with water for 2 hours, filter, wash, and evaporate the filtrate to a syrup. The syrup is then oxidized in the usual way.

The amounts of oxalic and mucic acid in mixtures of the pure acids can be determined by regulated oxidation with potassium permanganate.[1]

Determination of α-Cellulose.—The portion of cellulose fibers undissolved by a 17.5 per cent solution of sodium hydroxide represents α-cellulose. The α-cellulose from cotton cellulose is not immune to a second alkaline treatment, while that from wood may lose 4 to 7 additional per cent.[2] Pentosan is the chief constituent removed from wood cellulose. The determination is influenced by such factors as fineness of the sample, proportion of alkali to cellulose, temperature, and extent of dilution before filtration whereby colloidal cellulose is precipitated.[3] It is frequently almost impossible to filter the α-cellulose from cellulose obtained by the chlorination of wood powder (80 to 100 mesh). The method used by the writer is given below.

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[1] E. O. Whittier, *J. Am. Chem. Soc.*, **45** (1923), 1391.

[2] C. G. Schwalbe and E. Becker, *Zellstoff u. Papier*, **1** (1921), 93–94.

[3] P. Waentig, *Zellstoff u. Papier*, **2** (1922), 12–18.

Procedure.—The sodium hydroxide solution is prepared by dissolving the alkali in an equal weight of water and allowing it to stand several days for the sodium carbonate and other impurities to settle. The clear supernatant liquid is decanted, diluted with an equal volume of water free from carbon dioxide, cooled to room temperature, and its strength determined by titration. It is then diluted to give a solution containing 17.5 per cent by weight of sodium hydroxide.

Place 1 gram of the dry sample in a 250-cubic-centimeter beaker, add 25 cubic centimeters of 17.5 per cent sodium hydroxide solution, mix thoroughly with a glass rod, cover with a watch glass and let stand 30 minutes. Dilute with 25 cubic centimeters of water and filter through a tared alundum crucible. Wash the residue with 50 cubic centimeters of 8 per cent sodium hydroxide solution, then with water, 1 per cent acetic acid, and finally with water until the filtrate is neutral to methyl red. The crucible is then dried and weighed.

The α-cellulose determination with strong sodium hydroxide is not satisfactory for wood cellulose. It will probably be replaced by a method based on the use of boiling, dilute alkali.[1]

The following procedure has been recommended, particularly for determining the value of a pulp for viscose:[2] 3.5 grams of pulp are dried at 105°, weighed, placed in a porcelain mortar, 50 cubic centimeters of 17.5 per cent sodium hydroxide added, and triturated to a uniform paste with a pestle. After standing 45 minutes, the paste is diluted with 50 cubic centimeters of water, and transferred to a Büchner funnel, 8 to 10 centimeters in diameter, provided with a fine muslin filter. The cellulose is washed with 200 cubic centimeters of 8 per cent sodium hydroxide, sucked dry, washed with 50 cubic centimeters of 5 per cent acetic acid, and sucked dry. The pulp is now transferred to the mortar triturated with 50 cubic centimeters of 5 per cent acetic acid, filtered, washed until neutral to litmus paper, and dried. The results are 2 to 3 per cent lower than by the usual method.

The precipitate obtained on acidifying the alkaline filtrate from the α-cellulose is the β-cellulose and the portion remaining in solution is the γ-cellulose. Except under special circumstances, the determination of β- and γ-cellulose may well be neglected, since the data are of no particular value. A good volumetric method for determining α-, β-, and γ-cellulose, based on oxidation with chromic acid, has been devised by Bray and Andrews.[1]

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[1] *Cf.* E. G. Parker, *J. Phys. Chem.*, **17** (1913), 219–229.

[2] P. Waentig, *Zellstoff u. Papier*, **2** (1922), 225–228.

The determination of "wood gum"[2] is another procedure of no special value and may be supplanted by the determination of α-cellulose.

Baryta Resistance Value.[3]—Three grams of the air-dry sample are placed in an Erlenmeyer flask and 200 cubic centimeters of barium hydroxide solution, saturated at room temperature, are added. The flask is attached to a reflux condenser and the contents boiled gently for 1 hour. The pulp is filtered hot in a Gooch crucible, washed with hot water, 1 per cent hydrochloric acid, and then with water until free from acid. The residue is dried for 4 hours at 105° and a correction applied for the ash.

The baryta resistance value is not equivalent to the α-cellulose determination, but is capable of more exact control than the latter. Sulphite pulps give lower values than for α-cellulose, while pulps prepared or purified with alkalis may give higher values. The two methods give practically equivalent results when applied to specially purified sulphite pulps (Edelzellstoffe). About one-third of the pentosans are removed by treatment with barium hydroxide, while two-thirds are removed with a 17.5 per cent solution of sodium hydroxide. The baryta treatment has little effect on lignin but more of this constituent is removed from Mitscherlich pulp than from Ritter-Kellner pulp. The reducing substances are largely destroyed.

Copper Number.—The reducing action of cellulose is due to impurities such as lignin and carbonyl groups produced by the oxidation or hydrolysis of cellulose. Kollmann[4] used potassium permanganate to determine the reducing properties. The most serviceable reagent is Fehling's solution, which was employed by

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[1] M. W. Bray and T. M. Andrews, *J. Ind. Eng. Chem.*, **15** (1923), 376.

[2] H. Kast, "Untersuchung der Spreng- und Zündstoffe" (1909), 919; C. Piest, "Die Cellulose" (1910), 122; M. Freiberger, *Z. anal. Chem.*, **56** (1917), 299.

[3] C. G. Schwalbe and H. Wenzl, *Zellstoff u. Papier*, **2** (1922), 75; *cf.* C. G. Schwalbe and E. Becker, *Ibid.*, **1** (1921), 100.

[4] L. Kollmann, *Papier-Fabr.*, **8** (1910), 863, 890.

Vignon.[1] The application of this reagent, largely developed by Schwalbe,[2] has undergone many modifications[3] in an attempt to secure consistent results. According to Hess,[4] the Schwalbe method is not applicable to celluloses soluble in alkali, owing to their sensitiveness to hot alkali. He gives a modified procedure.

The method given below is due to Staud and Gray.[5]

Solutions.—(*A*) Copper sulphate crystals are washed to remove extraneous matter and dried; 137 grams of $CuSO_4.5H_2O$ are dissolved in distilled water and made up to 2 liters. (*B*) 692 grams of potassium sodium tartrate, which has been recrystallized from warm water and dried at room temperature, are dissolved in approximately 1 liter of water. To this, are added 200 grams of sodium hydroxide and the solution made up to 2 liters. The sodium hydroxide is prepared by making a saturated solution and allowing it to stand for 10 days. A sample is then pipetted out and titrated with standard hydrochloric acid. The volume of the solution containing 200 grams of sodium hydroxide is then calculated and used.

Ferric Ammonium Alum Solution.—One hundred grams of ferric ammonium alum, $(NH_4)_2SO_4.Fe_2(SO_4)_3.24H_2O$, is placed in 700 cubic centimeters of water and 140 cubic centimeters of concentrated sulphuric acid added. When clear, the solution is made up to 1 liter.

Preparation of Sample.—Paper is cut into pieces 2 to 5 millimeters square. Cotton linters require no treatment. Raw cotton, sliver, and standard cellulose are first pulled apart and then cut finely. Pulp fibers are freed by shaking the pulp in the presence of water and glass beads in a wide-mouthed glass-stoppered bottle.

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[1] L. Vignon, *Compt. rend.*, **125** (1897), 448.

[2] C. G. Schwalbe, *Ber.*, **40** (1907), 1347; *Z. angew. Chem.*, **23** (1910), 924; **27** (1914), 567; "Die Chemische Betriebskontrolle in der Zellstoff- und Papierindustrie," 2nd ed., Berlin (1922), 230.

[3] M. Freiberger, *Z. angew. Chem.*, **30** (1917), 121; E. Hägglund, *Papier-Fabr.*, **17** (1919), 301; E. Knecht and L. Thompson, *J. Soc. Dyers Colourists*, **36** (1920), 255; H. Braidy, *Rev. gén. mat. col.*, **25** (1921), 35; Koehler and Marqueyrol, *J. Soc. Chem. Ind.*, **41** (1922), 323A; E. Benesch, *Chem. Ztg.*, **48** (1924), 861; D. A. Clibbens and A. Geake, *J. Textile Inst.*, **15** (1924), 31T.

[4] K. Hess *et al.*, *Ann.*, **440** (1924), 290–304.

[5] C. J. Staud and H. L. Gray, *J. Ind. Eng. Chem.*, **17** (1925), 741.

Procedure.—The sample weighing 3 grams, less if possessing high reducing properties, is placed in a 1.5-liter balloon flask equipped with a short reflux condenser and stirrer. Into the top of the condenser, is inserted a small, short-stemmed funnel through which passes the shaft of the stirrer. The flask is then placed in a bath at 100°.

In another 1.5-liter balloon flask, are placed 350 cubic centimeters of water, allowance being made for any water introduced in disseminating a sample by shaking with beads, 20 cubic centimeters of copper sulphate solution, and 30 cubic centimeters of alkaline tartrate solution. The contents of the flask are heated to 100° and added to the sample in the other flask. The flask is then heated in a water bath for 45 minutes with stirring sufficiently rapid to keep the contents in gentle motion. The flask is then removed and the solution immediately filtered on a Büchner funnel through two sheets of Whatman No. 5 filter paper. The material on the filter is washed first with 1 liter of cold water and then with 750 cubic centimeters of boiling water.

The Büchner funnel is then transferred to a 250-cubic centimeter filter flask. The contents are treated with 25 cubic centimeters of ferric alum solution, in the case of standard cellulose; materials having a higher copper number, or fine texture, may require more ferric alum to remove the cuprous oxide. In such cases, it is added in 25-cubic-centimeter portions and a blank determined to correct for the additional ferric alum. The ferric alum retained by the material is washed out with 100 cubic centimeters of $2N$ sulphuric acid, applied in two 50-cubic-centimeter portions. The Büchner funnel is then removed and the contents of the flask titrated to a light pink with $0.04N$ potassium permanganate.

$$\frac{\text{Cubic centimeters } KMnO_4 \text{ used} \times 0.00254 \times F \times 100}{\text{Weight of sample}} = \text{copper number.}$$

$$1 \text{ cubic centimeter } 0.04N\ KMnO_4 = 0.00254 \text{ gram copper.}$$

$$F = \text{factor of } KMnO_4.$$

Standard cellulose prepared from cotton has a copper number of 0.0045. As a method of general utility, the copper number has still to justify its existence.

Determination of Oxycellulose.—One gram of air-dry cellulose is suspended in 50 cubic centimeters of distilled water and titrated with $0.01N$ sodium hydroxide solution. A sharper end point is obtained with phenolphthalein, at a temperature of 80°, than with litmus. Complete neutralization of the difficultly soluble acids requires several hours. In the case of oxycelluloses prepared with bleaching powder, the acidity is slight, since the acids are largely present as their calcium salts. It is necessary to incinerate a portion of the sample and add the alkalinity of the ash to the titration figure.[1] Samples requiring more than 10 cubic centimeters of alkali may be considered as containing oxycellulose. Titration values for several modified celluloses are given on page 279.

Great care should be exercised with oxycelluloses prepared with acid oxidizing agents to obtain them free from mineral acids. The colloidal oxycellulose prepared with nitric acid is obtained free from nitric acid only after prolonged dialysis.

According to Becker,[2] when oxycellulose is shaken with a solution of barium hydroxide for several hours, then thoroughly washed, a barium compound of oxycellulose remains in the cellulose. The barium is removed by washing with dilute hydrochloric acid and determined in the filtrate as barium sulphate. The amount of barium retained is an indication of the amount of oxycellulose.

	Barium, Per Cent
Oxycellulose by $Ca(ClO)_2$	2.18
Oxycellulose by $KMnO_4$	1.46
Oxycellulose by H_2O_2	0.34
Normal bleached sulphite pulp	0.20
Overbleached sulphite pulp	0.84
Hydrocellulose (Girard)	0.10
Hydrocellulose (Lederer)	0.17
Cotton	0.02

Oxycellulose cannot be determined by means of *p*-nitrophenylhydrazine, since only adsorption compounds are formed.[3]

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[1] C. G. Schwalbe and E. Becker, *Ber.*, **54** (1921), 545.

[2] E. Becker, *Zellstoff u. Papier*, **1** (1921), 5.

[3] E. Knecht and L. Thompson, *J. Soc. Dyers Colourists*, **36** (1920), 254.

The reducing action of oxycellulose on vat dyes has also been employed for its determination.[1] Nishida[2] used a method based on the affinity of oxycellulose for methylene blue, 1 gram of oxycellulose being equivalent to 0.06276 gram of the dye. The excess methylene blue was determined by titration with titanium chloride. According to Kita,[3] the method is untrustworthy, since the amount of dye taken up is dependent on the fineness of the sample, and no proportionality exists between the quantity of methylene blue absorbed and the amount of oxycellulose present.

The pink color developed when oxycellulose is shaken with a solution of sodium chloride containing methyl orange is a good qualitative test.

There is no method known for the absolute quantitative determination of oxycellulose, since it is an indefinite substance. An attempt in this direction is the method of Lenze.[4] The pulp is extracted three times with 17 per cent sodium hydroxide, the filtrate neutralized with nitric acid, and sufficient 20 per cent nitric acid added to give a 5 per cent solution. The solution is heated in a water bath for 3 hours, the precipitate collected, washed with water, dried, and weighed.

The method is based on the supposition that all the hemicelluloses are rendered soluble by the acid treatment and that the insoluble portion is oxycellulose. Hydrocellulose and similar forms of cellulose giving a colloidal solution with the alkali would behave as oxycellulose.

Aside from the absence of carboxyl groups, hydrocellulose has no properties that distinguish it clearly from oxycellulose.

Preparation of Standard Cellulose.—A committee[5] of the Division of Cellulose Chemistry, American Chemical Society, recommended that the cotton be boiled in a solution of sodium resinate and subsequently bleached. Corey and Gray[6] have suggested certain desirable modifications, including abandonment of bleaching.

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[1] R. Scholl, *Ber.*, **44** (1911), 1312; W. F. Ermen, *J. Soc. Dyers Colourists*, **28** (1912), 132.

[2] H. Nishida, *Kunststoffe*, **4** (1914), 266.

[3] G. Kita, C. A., **11** (1917), 2405.

[4] F. Lenze, B. Pleus, and J. Müller, *J. prakt. Chem.*, **101** (1920), 259.

[5] *J. Ind. Eng. Chem.*, **15** (1923), 748.

[6] A. B. Corey and H. L. Gray, *J. Ind. Eng. Chem.*, **16** (1924), 853, 1130.

The apparatus required is illustrated by Fig. 12. The nickel-screen (24-mesh) container is 6.5 inches high and 5 inches wide. It is suspended from a nickel chain attached to a mechanical stirring device giving an up-and-down movement to obtain circulation of the alkali through the cotton.

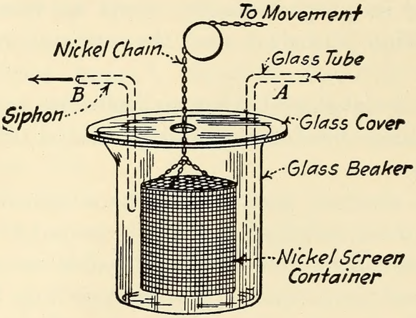

Fig. 12.—Apparatus for preparing standard cellulose. *A* represents a bent glass tube through which wash water is added to displace the liquid. *B* is a siphon. *A* and *B* are removed when the cellulose is boiled.

Procedure.—Remove by hand all visible impurities in 75 grams of Wannamaker's Cleveland raw cotton. Extract it in a Soxhlet apparatus for 6 hours with 95 per cent alcohol; follow by extraction with ether for 6 hours.

Place the cotton in the nickel basket, and add 3000 cubic centimeters of a 1 per cent solution of sodium hydroxide which has been previously boiled to expel air. Boil for 10 hours, during which time 10 liters of fresh 1 per cent sodium hydroxide are introduced. This is accomplished by having a flask containing the solution, which is maintained at the boiling point, at such a level that the liquid may be siphoned into the beaker containing the cotton. The fresh solution enters at the bottom of the beaker, while the old solution is removed from the top by a constant-level overflow. The rate of flow is regulated so that it takes 10 hours for the fresh solution to flow in. By this method the products extracted by the solution are continuously removed.

When the solution in the flask is nearly gone, add a small portion of distilled water which has been boiled. Repeat this operation several times, fill the flask with boiled water, and wash the cotton in this manner. Add water continuously in this way until the cotton is thoroughly washed. Thus during the period of treatment and washing, the cellulose is not exposed to air. Drain the cellulose and remove it from the container. Transfer it to a Büchner funnel and wash with three changes of distilled water, using suction. Immerse the cotton in a 1 per cent solution of acetic acid for 2 hours and then wash with four changes of distilled water. Permit the cotton to dry in the air.

The standard cellulose will contain about 99.8 per cent of α-cellulose and 0.05 per cent of ash.

Determination of the Bleach Requirement of Pulps.—A number of methods, based for the most part on the use of oxidizing agents, have been developed for estimating the amount of chlorine necessary to bleach a pulp. There may be mentioned: titration of the oxides of nitrogen evolved when the pulp is heated with nitric acid;[1] absorption of iodine from a standard solution;[2] weight of chlorine gas absorbed;[3] volume of chlorine gas absorbed;[4] titration of the hydrochloric acid formed on chlorination;[2] reduction of potassium permanganate,[5] sodium bromate,[6] and bleaching powder.[7]

Tingle Bromate Method.[8] *Bromate Solution.*—Add 8 grams of bromine to 100 cubic centimeters of N sodium hydroxide solution, agitate until solution is complete, and boil. The sodium hypobromite is converted to sodium bromate. Standardize by adding potassium iodide to a known volume, acidifying with hydrochloric acid, and titrating the liberated iodine with $0.1N$ sodium thiosulphate solution.

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[1] F Seidel, "Studien über den Zellulosedarstellungsprozess und eine Methode für Bestimmung des Reinheitsgrades von Zellulosen," Diss. Dresden (1907); E. Richter, *Papier-Fabr.*, **43** (1912), 1631; **45** (1914), 2021.

[2] E. Richter, *Papier-Fabr.*, **43** (1912), 1631.

[3] P. Waentig and W. Gierisch, *Z. angew. Chem.*, **32** (1919), 173.

[4] R. B. Roe, *J. Ind. Eng. Chem.*, **16** (1924), 808.

[5] B. Johnsen and J. L. Parsons, *Zellstoff u. Papier*, **2** (1922), 258; H. Roschier, *Ibid.*, 184.

[6] A. Tingle, *J. Ind. Eng. Chem.*, **14** (1922), 40; T. M. Andrews and M. W. Bray, *Ibid.*, **9** (1923), 934.

[7] P. Klemm, *Wochbl. Papierfabr.*, **40** (1909), 3973; R. Sieber, *Zellstoffchem. Abhandl.*, **1** (1920), 53; *Zellstoff u. Papier*, **1** (1921), 181–184; **2** (1922), 27–29.

[8] T. M. Andrews and M. W. Bray, *l.c.;* A. Tingle, *l.c.*

Acid Solvent.—Into a flask containing 450 cubic centimeters of hydrochloric acid (sp. gr. 1.19), pour slowly 50 cubic centimeters of sulphuric acid (sp. gr. 1.84). Mix thoroughly, cool, and store in a cool place.

Procedure.—Place 0.6 to 0.75 gram of dry pulp in a glass-stoppered, 500-cubic-centimeter bottle. Add 30 cubic centimeters of the acid solvent and shake occasionally until the pulp is dissolved. About 30 minutes are required. Hard pieces may be disintegrated with a glass rod. Bring the temperature of the solution to 23°, add 300 cubic centimeters of water having the same temperature, and shake thoroughly. Add 10 cubic centimeters of the bromate solution so that it will run down the side of the bottle, stopper, shake well, and allow to stand 20 minutes at a temperature of 23° with occasional gentle shaking. Stop the oxidation by adding 2 grams of potassium iodide dissolved in 25 cubic centimeters of water and titrate at once with $0.1N$ sodium thiosulphate solution. Use starch as the indicator when the iodine is nearly exhausted. Towards the end, the thiosulphate should be added slowly on account of the iodine adsorbed by the pulp. The end point is reached when the pulp appears white or cream colored.

The "chlorine number" represents the weight of chlorine reacting with 100 parts of oven-dry pulp.

$$\text{Chlorine number} = \frac{100 \times A \times B}{X}.$$

A = 0.00355 gram, the weight of chlorine in 1 cubic centimeter $0.1N$ solution.
B = cubic centimeters of $0.1N$ bromate solution consumed.
X = weight of pulp.

The actual weight of chlorine required to bleach 100 parts of pulp is obtained by multiplying the "chlorine number" by an empirical factor K. The latter has been found to be 3 for sulphite pulp, and varies from 3.6 to 4.9 for soda pulps. It is necessary to determine K for each class of pulp under the bleaching conditions obtaining in the mill.

In spite of running the digesters under apparently uniform conditions, there is usually considerable variation in the bleach requirements of the pulps from the several digesters. This is remedied in part by mixing the pulp from several cooks before bleaching.

Roe Chlorine Method.[1] *Apparatus* (Fig. 13).—The burette *A* is a modified Morehead gas burette, calibrated in 0.2 cubic centimeter from 0 to 100 cubic centimeters, and provided with a three-way cock *C* at the top, and an ordinary cock *K* at the bottom. The burette is surrounded by an air jacket *B*. The top capillary of the burette is provided with a No. 8 rubber stopper and a small one immediately above it. The water jacket *D*, consisting of a wide-mouth, 8-ounce bottle with the bottom removed, fits over the large stopper. The reaction bulb *E* must be of special size and form (a Hortvet tube serves the purpose

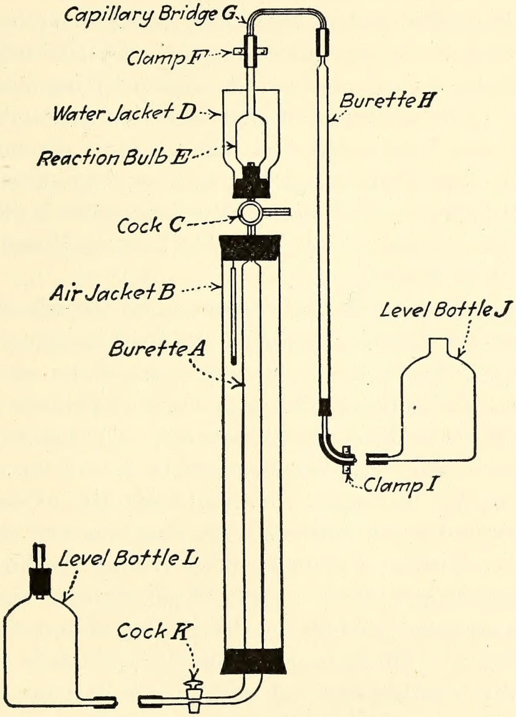

FIG. 13.—Apparatus for determining the chlorine absorption by unbleached sulphite pulp. (*After Roe.*)

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[1] R. B. ROE, *J. Ind. Eng. Chem.*, **16** (1924), 808.

very well if the graduated or constricted portion is cut off about 1 centimeter from the bottom). The reaction bulb is connected by rubber tubing with a capillary bridge *G*. A screw clamp is placed between the end of the reaction bulb and the capillary bridge. The other end of the bridge is connected by rubber tubing with the bottom end of an inverted Mohr burette *H*. The other or larger end of the Mohr burette is connected by means of a cork, and glass and rubber tubing with the level bottle *J*. A screw clamp *I* operates on the rubber tubing leading to the level bottle. The lower end of burette *A* is connected by rubber tubing with the level bottle *L*. The latter is provided with a stopper and rubber tubing leading to a hood or other source of positive ventilation. The level bottle *L* contains a filtered solution of calcium chloride of 32° Bé. The burette *H* and the bottle *J* are filled with water.

Procedure.—The jacket *D* is removed and the reaction bulb *E* allowed to swing down by means of the flexible connections with the bridge *G*. Stopcock *C* is first opened to communicate through the side capillary with a cylinder of chlorine. Cock *K* is opened and the chlorine gas liberated. The gas is allowed to force the liquid in the burette down and back into the level bottle and bubble slowly through it for about 1 minute. Cock *C* is then turned to communicate both with the side arm and the air, and the gas in the burette is forced out by raising the bottle. It is not customary to cut off the supply of gas while so doing. This operation is repeated, and on the third filling of burette *A* the gas supply is closed at the cylinder when the level falls between 90 and 100 cubic centimeters. A short piece of bent, drawn-out glass tubing is inserted into that portion of the capillary above cock *C* and the chlorine blown out. The gas in burette *A* is then leveled up, but not accurately.

Exactly 2 grams of oven-dry pulp in the form of thin sheets is weighed out. The sample is then immersed in water for a few seconds until saturated, removed, squeezed between blotters by hand, and again placed on the balance. Sufficient water is added to make the total weight 4.5 grams. The sample is then placed in the reaction bulb, each piece being slightly crumpled. When the whole sample is in the tube, a short piece of flexible wire with a small hook on the end is inserted, and the sample pulled down so that the upper third of the enlarged space in the reaction bulb is empty. The water jacket *D* is next fitted to its stopper and the reaction bulb also firmly fitted to the smaller stopper. The water jacket is filled with water previously brought to 25°. Stopcock *C* is then opened so as to communicate with the burette and reaction bulb. The gas is carefully leveled and the volume read. The level bottle *L* is raised slightly and placed on a stand so as to put the gas under slight pressure. Screw clamp *I* is opened and exactly on the even minute clamp *F* is slowly opened. The water level in burette *H*, which previously had been brought to some definite place in the capillary bridge, is allowed to fall slowly until about 10 cubic centimeters of air have been drawn into burette *H*, when clamp *F* is closed. The water in burette *H* is leveled with bottle *J*, and clamp *I* tightened. The level in burette *A* will gradually rise, and during the first 5 minutes the liquid is leveled up frequently, cock *K* being closed during the intervals between leveling. This maintains the gas approximately under atmospheric pressure. The reaction proceeds very rapidly at first, but after 5 minutes the rate of increase is quite slow. Exactly 14 minutes from the time clamp *I* was opened, the water in burette *H* is forced up, clamp *I*, cock *K*, and clamp *F* being opened in the order named. When the water reaches the initial point in the bridge, clamps *F* and *I* are closed and the gas volume is immediately leveled and read.

The blank amounting to 0.40 per cent is subtracted, and the difference, expressed in grams of chlorine absorbed by 100 grams of oven-dry pulp, is the "chlorine number."

After each determination, the water in jacket *D* is siphoned off and the jacket and the reaction bulb each disconnected from its respective stopper. The chlorinated pulp is removed from the bulb, and the latter wiped dry on the inside with a cloth. A piece of glass tubing is run into the bulb and any residual chlorine is blown out. The time consumed for a single determination is about 20 minutes. The average percentage error is 0.8 per cent.

WEIGHT OF A LITER OF CHLORINE AT 25° AND VARIOUS PRESSURES

Pressure, in millimeters.......	735	740	745	750	755	760
Weight, in grams............	2.8071	2.8260	2.8450	2.8642	2.8833	2.9122

Differentiating Unbleached Sulphite from Sulphate Pulp.[1] Solution *A*.—Dissolve 2 grams of malachite green in 100 cubic centimeters of distilled water.

Solution *B*.—Dissolve 1 gram of fuchsine (basic) crystals in 100 cubic centimeters of distilled water.

Use one part of malachite green with two parts of the fuchsine solution. Place 2 drops of the mixture on the fibers, leave for 2 minutes, then rinse with 4 drops of a dilute solution of hydrochloric acid made by adding 1 cubic centimeter of concentrated hydrochloric acid (sp. gr. 1.19) to 1 liter of water. Allow the acid solution to remain on the fibers for 10 seconds. Remove the excess acid solution with filter paper, apply a few drops of distilled water, and remove the water with filter paper. Under the microscope, unbleached coniferous sulphite pulp will appear violet, and unbleached coniferous sulphate pulp green.

The solutions should be mixed just previous to use and the stains should be checked on authentic samples of pulp.

Differentiating Sulphite from Soda Pulp. *Alexander's Stain.*[2]—This stain consists of three solutions:

I. 0.2 gram congo red.
   300 cubic centimeters distilled water.
II. 100 grams calcium nitrate.
   50 cubic centimeters distilled water.
III. Herzberg's stain made up as follows:
   A. 20 grams zinc chloride.
      10 cubic centimeters water.
   B. 2.1 grams potassium iodide.
      0.1 gram iodine.
      5 cubic centimeters water.

Add *B* to *A* and prepare in the usual way.

The sample to be tested is first stained with 2 drops of the congo red solution for 1 minute, after which the excess dye is carefully removed with a blotter and the sample allowed to dry.

The dry, stained sample is then immersed in 3 drops of the calcium nitrate solution and allowed to remain for 1 minute. At the end of this time, 1 drop of Herzberg's stain is added, the whole quickly and thoroughly mixed, and the cover glass put in place.

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[1] R. E. Lofton and M. F. Merritt, *Bur. Standards, Tech. Paper*, **189** (1921).

[2] E. P. Cameron, *Paper*, **33,** 26 (1924), 138.

The slide may be examined immediately, but there seems to be a slightly stronger tone to the colors if it is allowed to stand for 3 or 4 minutes before examination. The sulphite should be evenly stained pink and the soda deep blue. The vessels in a hardwood soda pulp are the hardest portion to stain properly, and if these give a good color closely resembling that of the soda fiber the stain is working very well.

Wasicky[1] uses gentian violet. Alcohol removes this dye from soda pulp but not from sulphite pulp.

Sieber[2] distinguishes sulphate from sulphite pulp though the greater resistance of the former to baryta solution.

Some methods are based on the resin content. Klemm[3] uses a saturated solution of Sudan III in three parts of alcohol and one part of water. Before use, two parts of this solution are mixed with one part of glycerine. The medullary ray cells of sulphite pulp are stained red, while the corresponding cells in soda and sulphate pulp are not dyed. The reagent is useful as a qualitative test for resin in sulphite pulp to determine if sufficient resin is present to cause trouble on the screens during the manufacture of paper.[4]

The resin from sulphite pulp gives the cholesterol reaction, while that from soda pulp does not.[5] Place in a test tube about 0.5 gram of the pulp and 1 to 2 cubic centimeters of chloroform or carbon tetrachloride. Heat to boiling, filter into a test tube, add 0.5 cubic centimeter of acetic anhydride to the filtrate, then 6 to 10 drops of pure concentrated sulphuric acid, so that the sulphuric acid forms a layer at the bottom of the tube. The extract from sulphite pulp gives a rose-red color, changing to green on adding more sulphuric acid. Only a dirty-yellow color is obtained with soda pulp.

The reaction cannot be definitely attributed to a sterol, since rosin and terpenes behave similarly. These constituents are normally almost completely removed from slightly resinous woods by an alkaline cook.

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[1] R. Wasicky, *Papier-Fabr.*, **16** (1918), 212, 228.

[2] R. Sieber, *Papier-Fabr.*, **21** (1923), 453; *cf.* Finkelstein and Schwarz, *Ibid.*, **16** (1918), 291.

[3] P. Klemm, *Wochbl. Papierfabr.*, **48** (1917), 2159.

[4] P. Klemm, *Wochbl. Papierfabr.*, **42** (1911), 967.

[5] C. G. Schwalbe, *Wochbl. Papierfabr.*, **36** (1906), 2640.

Differentiating Bleached from Unbleached Sulphite Pulp.[1]—The method is based on the formation of Prussian blue when lignified fibers are treated with a solution of ferric ferricyanide. The green or blue color is intensified by staining red.

Ferric Ferricyanide Solution. Solution *A*.—Dissolve 2.7 grams of ferric chloride ($FeCl_3.6H_2O$) in water and make up to 100 cubic centimeters.

Solution *B*.—Dissolve 3.29 grams of potassium ferricyanide in water and make up to 100 cubic centimeters. Both solutions should be filtered.

Substantive Red Solution.—To 100 cubic centimeters of hot water, add 0.4 gram of benzopurpurin 4B extra (Bayer) and 0.1 gram of oxamine brilliant red BX (Badische).

Mix equal volumes of solutions *A* and *B* in a beaker, heat to 35°, insert the slide containing the moist fibers, and maintain at the above temperature for 15 minutes. Remove the slide, dip it into distilled water six times, and repeat the procedure in fresh water. Place the slide in the substantive red solution, heated to 45°, and leave 5 minutes; then rinse. Unbleached fibers are stained blue, and the bleached red.

Herzberg Iodine Stain.[2] Solution *A*.—Dissolve 50 grams of dry zinc chloride (fused sticks) in 25 cubic centimeters of distilled water measured from a pipette. The specific gravity must be adjusted to 1.8. Pour 40 cubic centimeters of the solution into a tall cylinder.

Solution *B*.—Dissolve 5.25 grams of potassium iodide and 0.25 gram of iodine in 12.5 cubic centimeters of water.

Add solution *B* to *A*, mix well, and place it in the dark. The following day pipette off the clear portion into a black bottle, leaving 3 or 4 cubic centimeters of the stain above the sediment. Add a leaf of crystalline iodine. Where color differentiations are important, the stain should not be used longer than 2 weeks. Rag, cotton, linen, and hemp are colored wine red or brownish pink; chemical wood pulp, bleached straw, and jute a dark blue; mechanical wood pulp, unbleached jute, and straw generally a lemon yellow; esparto bluish or reddish; and manila almost any shade from blue to yellow.

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[1] C. G. Bright, *J. Ind. Eng. Chem.*, **9** (1917), 1044.

[2] M. F. Merritt, *Paper Trade J.*, **75**, 8 (1922), 43–44; *Bur. Standards, Tech. Paper*, **250** (1924), 103.

The blue coloration which iodine imparts to carbohydrates, as well as to such compounds as basic lanthanum acetate,[1] is an adsorption phenomenon. When carbohydrates have a relatively low dispersion, the color is blue, and when a high dispersion brownish red.[2]

Mangin[3] examined a large number of salts and found that iodine in a concentrated solution of many of them stained cellulose. The most suitable were $AlCl_3$, $CaCl_2$, $MnCl_2$, $MgCl_2$, $SnCl_2$, $Ca(NO_3)_2$, and $Zn(NO_3)_2$. The zinc chloride reagent was the most sensitive.

Lignin Reagents. *Phloroglucinol.*—Lignocellulose is stained a magenta or wine color. Dissolve 5 grams of phloroglucinol in 125 cubic centimeters of distilled water and 125 cubic centimeters of concentrated hydrochloric acid. Keep the solution in a dark place.

Owing to the deterioration of the above solution, it is preferable to make a stock solution of 2 grams of phloroglucinol in 100 cubic centimeters of 95 per cent alcohol. Two volumes of the alcohol solution are diluted with 1 volume of concentrated hydrochloric acid as needed.

Paranitraniline.—A saturated solution of this compound in concentrated hydrochloric acid stains lignified fibers orange yellow.

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[1] W. BILTZ, *Ber.*, **37** (1904), 719.

[2] E. HERZFELD and R. KLINGER, *Biochem. Z.*, **107** (1920), 273.

[3] L. MANGIN *Bull. soc. botan. France,* **35** (1888), 421–426.

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[1] For synonomy of scientific and common names of North American trees see G. B. Sudworth "Check List of the Forest Trees of the United States." Bull. 17, U. S. Dept. Agr., Division of Forestry, Washington (1898).

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